PB91-148460

Ecological Exposure and Effects of Airborne Toxic Chemicals: An Overview

(U.S.) Corvallis Environmental Research Lab., OR

Jan 91

U.S. Department of Commerce
National Technical Information Service
NTIS

PB91-148460

EPA/600/3-91/001
January 1991

ECOLOGICAL EXPOSURE AND EFFECTS OF AIRBORNE TOXIC CHEMICALS: AN OVERVIEW

edited by

[1]Thomas J. Moser, [1]Jerry R. Barker, and [2]David T. Tingey

[1]ManTech Environmental Technology, Inc.
[2]US Environmental Protection Agency
Environmental Research Laboratory
200 S.W. 35th Street
Corvallis, Oregon 97333

NOTICE

The information in this document has been funded wholly (or in part) by the U.S. Environmental Protection Agency. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement of recommendation for use.

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before comple

1. REPORT NO. EPA/600/3-91/001	**2.**	**3.** PB91-148460
4. TITLE AND SUBTITLE Ecological Exposure and Effects of Airborne Toxic Chemicals: An Overview		**5. REPORT DATE** January 1991 **6. PERFORMING ORGANIZATION CODE**
7. AUTHOR(S) Thomas J. Moser, Jerry R. Barker, and David T. Tingey		**8. PERFORMING ORGANIZATION REPORT NO.**
9. PERFORMING ORGANIZATION NAME AND ADDRESS 1st two, NSI, ERL-Corvallis; Tingey, US EPA, ERL-Corvallis		**10. PROGRAM ELEMENT NO.** **11. CONTRACT/GRANT NO.**
12. SPONSORING AGENCY NAME AND ADDRESS US Environmental Protection Agency Environmental Research Laboratory 200 SW 35th Street Corvallis, OR 97333		**13. TYPE OF REPORT AND PERIOD COVERED** Published Report **14. SPONSORING AGENCY CODE** EPA/600/2

15. SUPPLEMENTARY NOTES
1990. U.S. Environmental Protection Agency, Environmental Research Laboratory, Corvallis, OR.

16. ABSTRACT

Since the release of the Environmental Protection Agency's (EPA's) toxic release inventory (TRI) estimates for 1987, there has been a heightened concern over the nation's air quality. Primarily, this concern has been directed at human health effects in industrial-urban areas. The fact that many airborne chemicals pose hazards to human health is only one aspect of the problem. The continued deposition of airborne toxic chemicals pose threats to both terrestrial and aquatic ecosystems, this discussion is limited to terrestrial vegetation.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT Release to Public	**19. SECURITY CLASS** *(This Report)* Unclassified	**21. NO. OF PAGES** 170
	20. SECURITY CLASS *(This page)* Unclassified	**22. PRICE**

EPA Form 2220-1 (9-73)

TABLE OF CONTENTS

Table of Contents ii

Preface iii

Atmospheric Transport of Toxic Chemicals and Their Potential Impacts on Terrestrial Vegetation: An Overview (Thomas J. Moser, Jerry R. Barker, and David T. Tingey) 1

Organochlorines and Polycyclic Aromatic Compounds in the High Arctic (Greg W. Patton and Terry F. Bidleman) 8

Air-Sea Exchange of Hexachlorocyclohexane in the Bering and Chukchi Seas (Daniel A. Hinckley, Terry F. Bidleman, and Clifford P. Rice) 20

Trace Metal Deposition and Cycling in Forested Ecosystems (Andrew J. Friedland) 32

Atmospheric Deposition of Trace Metals to Lichens and Effects of Trace Metals on Lichens (Thomas H. Nash III) 40

Fate and Effects of PAHs in the Terrestrial Environment: An Overview (Nelson T. Edwards) 48

Effects of Organic Chemicals in the Atmosphere on Terrestrial Plants (Jeffrey R. Foster) 60

Effects of Atmospheric Pollutants on Peatlands (Noel R. Urban) 90

Use of the PHYTOTOX Database to Estimate the Influence of Herbicide Drift on Natural Habitats in Agroecosystems (James E. Nellessen and John S. Fletcher) 102

Biological Markers in Environmental Sentinels to Establish Exposure to, and Effects of, Atmospheric Toxicants (John F. McCarthy and Timothy J. Tschaplinski) 107

Air Toxics Ecological Effects Research Recommendations (Noel R. Urban and Jerry R. Barker) 128

References 130

PREFACE

It is a fact that numerous anthropogenic sources emit a large variety and quantity of chemicals, many of them toxic, into the atmosphere. These chemicals are commonly referred to as air toxics with groupings in five broad categories: 1) synthetic industrial organics, 2) agricultural pesticides, 3) trace metals, 4) organometallic compounds, and 5) non-metallic inorganics. It is also a fact supported by scientific evidence that through atmospheric transport and deposition, toxic chemicals find their way to rural locations, as well as remote areas such as the Arctic, high-elevation forests, oceans, seas, and peatlands. Given the number and strength of air toxic emission sources with their subsequent atmospheric transport and deposition, an increasing concern is that adverse biological effects ranging from the biochemical to the ecosystem level of organization may be occurring.

The slow biodegradability of many toxic compounds allows them to remain ecologically harmful for long periods of time. The persistent nature of these compounds can result in adverse biological effects by the incorporation and accumulation into food chains and disrupting ecological processes. The effects from the chronic deposition of airborne toxic chemicals on various levels of ecosystem organization and their potential interaction with natural stresses (e.g., insects, drought, disease) to induce antagonistic to synergistic effects are unknown.

The publication of the U.S. Environmental Protection Agency's (EPA) Toxic Release Inventory for 1987 and 1988 has heightened the concern over the nation's air quality in regards to air toxics. Although this concern is primarily human health related, more attention is currently being devoted to potential environmental impacts from air toxics, as is evident by debates over amendments to the Clean Air Act.

Little information is available concerning the regional distribution, exposure (concentration, duration, frequency), bioavailability or potential effects of airborne toxics on sensitive biota and ecosystems. Research is needed to focus on documenting chronic/cumulative impacts and mitigating ecological problems which may result from the chronic, persistent environmental loading of a large array of airborne toxic chemicals. In this regard, a credible, scientific data base is needed to support the policy in the control of air toxics compounds and the listing of chemicals on the Toxic Release Inventory.

The purpose of this document is to provide an overview of the current knowledge of ecological exposure, fate and effects of airborne toxic chemicals, particularly at locations distant from emission sources. The document consists of 11 chapters that were prepared by scientists who were invited to participate in air toxics-ecological effects sessions at the following conferences: 1) Air Waste and Management Association, 82nd Annual Meeting (June 25-30, 1989, Anaheim, California, USA), 2) Society of Environmental Toxicology and Chemistry, 10th Annual Meeting (October 28 - November 2, 1989, Toronto, Ontario, Canada); and 3) Environmental Protection Agency/Air and Waste Management International Symposium on Measurement of Toxic and Related Pollutants (April 30 - May 3, 1990, Raleigh, North Carolina, USA).

The emphasis of this document is on airborne chemical exposure, fate and effects in terrestrial ecosystems, particularly vegetation. However, many of the concepts presented will apply also to aquatic ecosystems. Chapter 1 provides an introduction and overview of our knowledge of air toxic emission sources, atmospheric transport and deposition, and potential impacts on terrestrial vegetation. Chapters 2 and 3 are technical papers addressing the measurements of agricultural pesticides and other toxic organics in arctic air and water, and demonstrates the ability of the atmosphere to transport and deposit contaminants to environments far from emission sources. Chapter 4 provides an overview of the sources of trace metals in forest ecosystems, evidence implicating their atmospheric deposition, and their potential effects on soil processes. Chapter 5 discusses atmospheric deposition of trace metals and their potential effects on lichens which are important components of many terrestrial ecosystems. Chapter 6 provides a thorough overview of the sources, ambient concentrations and fate of polycyclic aromatic hydrocarbons in the terrestrial environment. Chapter 7 provides a broad overview of the atmospheric deposition, fate and effects of synthetic organics on terrestrial plants. Chapter 8 focuses on evidence of atmospheric transport and deposition of airborne toxic chemicals into peatland ecosystems, and the effects of acid deposition and airborne toxics on peatlands structure and function. Chapter 9 discusses the potential threat of herbicide drift to natural plant communities associated with agroecosystems, and the use of the PHYTOTOX data base to estimate the threat of specific herbicides on native nontarget plant species. Chapter 9 also demonstrates the paucity of scientific literature that addresses the ecological effects of airborne toxic chemicals on natural vegetation. Chapter 10 provides a thorough description of the potential applications, advantages and difficulties of using animal and plant biomarkers to evaluate and monitor the exposure and effects of air toxics. Finally, a concluding chapter presents research needs to document the effects of ecosystems exposure to airborne toxic pollutants.

ATMOSPHERIC TRANSPORT OF TOXIC CHEMICALS AND THEIR POTENTIAL IMPACTS ON TERRESTRIAL VEGETATION: AN OVERVIEW

Thomas J. Moser[1], Jerry R. Barker[1], and David T. Tingey[2]

ManTech Environmental Technology, Inc.[1]
U.S. Environmental Protection Agency[2]
U.S. EPA Environmental Research Laboratory
Corvallis, OR

INTRODUCTION

Numerous anthropogenic sources emit a large variety and quantity of toxic chemicals into the atmosphere. Through the processes of atmospheric transport and deposition, toxic chemicals have found their way into remote environments far from emission sources. Recent data strongly suggest that the enriched concentrations of several contaminants detected in the air, water, soil, and biota of rural and remote environments are the result of long-range atmospheric transport from sources located in temperate and sub-tropical latitudes of North America and Eurasia. Many of these chemicals are persistent, and they bioaccumulate and remain biologically harmful for long periods of time. Although air toxics have been primarily considered an urban health problem, there is increasing concern among scientists that adverse ecological impacts may result from their deposition into terrestrial ecosystems and the subsequent exposure of plants. The chronic exposure of vegetation to low concentrations of air toxics may result in sublethal effects such as decreased plant productivity and vigor, that may culminate in changes in plant communities and ecosystem structure, composition, and function.

Airborne pollutants can be broadly defined as any chemical occurring in the atmosphere that may pose a threat to human health or the environment. This broad definition includes an array of chemicals ranging from the well-studied criteria pollutants to the less-studied radiatively important trace gases. However, to provide a more focused definition for this paper, air toxics refers to the following groups of airborne substances: (1) synthetic industrial organics, (2) agricultural pesticides, (3) trace metals, (4) organometallic compounds, and (5) nonmetallic inorganics.

Since the release of the Environmental Protection Agency's (EPA's) toxic release inventory (TRI) estimates for 1987 (US EPA, 1989), there has been a heightened concern over the nation's air quality. Primarily, this concern has been directed at human health effects in industrial-urban areas. The fact that many airborne chemicals pose hazards to human health is only one aspect of the problem. The continued deposition of airborne toxic chemicals on a regional to global scale will impact public welfare if it results in adverse impacts to the structure and function of sensitive terrestrial and aquatic ecosystems. Although airborne toxic chemicals pose threats to both terrestrial and aquatic ecosystems, this discussion is limited to terrestrial vegetation.

EMISSION SOURCES

Airborne chemicals are emitted into the atmosphere from a large number and variety of point- and area-sources. Anthropogenic emissions emanate from industrial, urban, and agricultural sources such as chemical, metal, plastic, and paper/pulp industries; fossil fuel processing plants; motor vehicles and aircraft; municipal waste incinerators; agricultural practices such as pesticide usage and field burning; and small businesses such as dry cleaners. Emissions of toxic chemicals into the atmosphere may occur directly by the deliberate or inadvertent releases from industrial or urban sources, or indirectly through volatilization following the deliberate or accidental discharge of chemicals into water or soil resources. Also, considerable amounts of toxics enter the atmosphere from wind drift and volatilization after agricultural chemical applications.

Industry is probably the major anthropogenic source of airborne toxic chemicals. Approximately 65,000 chemicals are used worldwide for industrial purposes (Schroeder and Lane, 1988). Many of these chemicals eventually are emitted into the atmosphere. The 1987 TRI reported that industries within the United States emitted more than 1.2 billion kilograms of toxic chemicals into the atmosphere (US EPA, 1989). The TRI underestimated the actual air emissions as it did not include air emissions from numerous area sources (e.g., agriculture, households, motor vehicles), industrial categories such as petroleum tank farms, companies with less than 10 employees, or urban businesses (e.g., dry cleaners).

A secondary source of airborne toxics is the application of pesticides. Atmospheric loads of pesticide residues resulting from wind drift, as well as volatilization from soil and plant surfaces after their application to agricultural, forest, range, industrial, and household lands are also significant. More than 455 million kilograms of pesticide active ingredients are used annually on 16% of the total land area of the United States (Pimentel and Levitan, 1986). Agricultural lands account for approximately 75% of the pesticide usage in the United States. The knowledge of magnitude of pesticide active ingredients entering the atmosphere during and following application is limited, but is estimated to range between 30 and 55% (Waddel and Bower, 1988).

ATMOSPHERIC PROCESSES

When chemicals are airborne, they are subjected to the prevailing atmospheric conditions. Wind, precipitation, humidity, clouds, fog, solar irradiation, and temperature influence the environmental fate of air toxics (Bidleman, 1988; Schroeder and Lane, 1988). The complex reactions within the atmosphere that are driven by chemical processes such as hydroxyl scavenging or solar irradiation may result in the formation of products that can be as toxic, or more so, than the parent compounds. On the other hand, transformation reactions may also render a toxic substance harmless.

The atmosphere is a major pathway for the transport and deposition of the air toxics from emission sources to the terrestrial ecosystem receptors - vegetation and soil (Bidleman, 1988). The prevailing meteorological conditions and the physiochemical properties of the chemicals will dictate atmospheric residence times and deposition velocities to the receptors (Schroeder and Lane, 1988). Atmospheric residence times depend on such characteristics as mode and rate of emission, atmospheric transformations, physical state (gas, solid, liquid), particle size, and chemical reactivity (Schroeder and Lane, 1988). Thus, airborne pollutants may be deposited close to their sources in urban or agricultural ecosystems, or be carried great distances before being deposited into remote ecosystems.

The movement of airborne chemicals downwind from point sources has received a great amount of attention since the early 1900s when the damaging effects on vegetation that occurred within plumes were recognized (Gordon and Gorham, 1963). During the last 10 to 20 years, however, the phenomenon of long-range atmospheric transport has been documented in the wide distribution of anthropogenic contaminants on regional and global scales. Industrial organic compounds, trace metals, and pesticide residues have been detected in the vegetation of remote terrestrial ecosystems such as the Arctic (Thomas, 1986), Antarctic (Bacci et al., 1986), forests, (Eriksson, et al., 1989), and peatlands (Rapaport and Eisenreich, 1988).

ENVIRONMENTAL PARTITIONING AND VEGETATION EXPOSURE

Terrestrial plants are exposed to toxic chemicals through the environmental media of air, water, and soil. The atmosphere, however, is of prime importance because of its potential for pollutant dispersal on a regional-to-global scale, its ability to move pollutants rapidly, and its dynamic nature. After pollutant deposition to terrestrial ecosystems, the fate of the toxic compounds depends on their partitioning coefficients.

The environmental partitioning of pollutants within ecosystems will dictate their potential ecological impact to vegetation and other biota (Weinstein and Birk, 1989). For example, trace metals tend to accumulate on soil surfaces via their adsorption to organic matter. Trace metal accumulation may reduce plant growth and vigor through the disruption of nutrient uptake by the roots and decreased organic matter decomposition. Gaseous chemicals reside in the atmosphere with the potential to disrupt plant-leaf biochemical processes after absorption through the stomata or cuticle. Because of the lipophilic nature of many synthetic organics, the waxy cuticle of vegetation may accumulate high levels of these substances. Transfer of toxic chemicals among ecosystem compartments will occur. Trace metals may be absorbed by plant roots or deposited onto the leaves and then transferred to the soil through deciduous tissue loss and decay. Contaminants may be passed along food chains through herbivory with the potential for biomagnification. The deposition of airborne toxic chemicals into agricultural ecosystems has the potential to contaminate human food resources.

IMPACTS ON TERRESTRIAL VEGETATION

Scientists have recognized that airborne pollutants can adversely impact agricultural and natural plant communities by reducing plant production and altering successional pathways (MacKenzie and El-Ashry, 1989; Weinstein and Birk, 1989). Emissions of sulfur dioxide, hydrogen fluoride, trace metals, and other toxics from pulp and paper mills, ore smelters, and power plants have severely reduced vegetation cover, biodiversity, and ecosystem integrity downwind from point sources (Gordon and Gorham, 1963; Weinstein and Birk, 1989). In addition to local plume effects, atmospheric pollutants also can cause regional damage to plant communities through exposure to chemical oxidants such as ozone, peroxyacetyl nitrates, or acid precipitation (Guderian, 1985; MacKenzie and El-Ashry, 1989).

The potential biological effects of air toxics on terrestrial vegetation are numerous and are mediated through individual plants to the community and ecosystem (Weinstein and Birk, 1989). The type and magnitude of these effects will depend on the pattern of exposure (e.g., duration, concentration, frequency, season) individual plants receive, their sensitivity to the pollutant, and the phytotoxicity of the chemical. When an airborne toxic chemical is introduced into a plant community some plants will be more affected than others depending on individual tolerances endowed by their genotype, as well as their phenology and various modifying microclimatic variables. The sensitive plants or species are no longer able to compete adequately with the tolerant plants or species and will be partially or completely replaced. Those plants that do survive and persist in contaminated habitats are the result of their tolerance or microhabitat protection.

After pollutant absorption by the plants through the leaves or roots, biochemical processes are the first site of action of the pollutant. If enzymatic degradation detoxifies the pollutant, then no injury will occur. However, if enzymatic action cannot render the pollutant or its metabolites harmless, then alterations in plant metabolism may result in foliar injury, altered carbohydrate and nutrient allocation, and reduced growth and reproductive capability (Guderian, 1985). The degree of impact to the plant will depend on the toxicity of the pollutant and its exposure pattern. Acute exposures usually cause observable morphological damage, such as leaf lesions, stunted growth, or even death. Plant death resulting from acute exposure is usually localized when it does occur; resulting from an inordinate amount of toxic chemical exposure through an accidental release or pesticide wind drift.

However, chronic, sublethal exposures may not induce observable morphological damage, but rather alter biochemical pathways, which can result in decreased vigor and productivity, altered phenology, loss of tissue, or reduced reproductive potential. Altered physiological processes will cause a loss of vigor and render the plant more susceptible to insect damage or disease. Decreased reproduction will impact the population through the loss of new recruitments to the plant community. With continual exposure, even at sublethal concentrations, sensitive plant populations may decrease in numbers allowing tolerant species to become dominant. Thus, shifts in plant community structure and composition could result in decreased biological diversity and altered ecosystem functions.

Plant damage resulting from acute air toxic exposures are usually limited in time and space as a result of control technology and legislation. However, sublethal, long-term plant exposure to airborne pollutants may predispose vegetation to other natural stressors and induce damage or mortality. Even though air toxic damage may not cause permanent functional loss, the diversion of biochemical resources to repair the injury will inhibit normal plant functions. Thus, air-toxic-induced physiological stress may predispose a plant to other stressors such as frost, drought, insects, or disease. Some scientists propose that the widespread forest tree decline is not the result of a single agent, but an interaction among chronic exposures of air pollutants and natural stresses.

Air toxics may also indirectly affect vegetation by directly affecting other organisms that are critically associated with the plants. Soil microorganisms and invertebrates are critical in ecosystems for litter decomposition and nutrient cycling. An accumulation of trace metals within the "O" horizon of the soil may limit organic matter decomposition and nutrient availability to plants. Many plants rely on insects for pollination. Airborne pollutants from the use of insecticides can reduce nontarget insect populations, resulting in inadequate flower pollination and subsequent seed set.

The effects of air toxics on vegetation can be extended to the animals within the ecosystem (Schreiber, 1985). Reduced plant cover and habitat quality will result in animals being more susceptible to predation and disease. Adequate birthing sites may be reduced because of changes in vegetation structure and cover. Animal forage that is contaminated may result in decreased population size or starvation. Toxic chemicals may be passed along food chains with the potential to reduce the health of herbivores or may bioaccumulate within predators. Animal populations will respond to such habitat changes through decreased reproduction, emigration, or mortality. Even though the populations of certain species may increase because of favorable habitat changes, the biological diversity of the overall ecosystem still may decrease.

RESEARCH NEEDS

Air toxic chemicals introduced into plant communities can produce effects ranging from the biochemical level to changes in plant community structure and composition. The effects of acute exposure to plants are well documented. However, a paucity of information exists on the effects of long-term, chronic exposures of air toxics to vegetation. The following areas of research would provide data to quantify vegetation responses to chronic air toxic exposure.

- Identify and prioritize the most critical airborne contaminants and sensitive ecosystems. A comprehensive computer-based system would be useful for conducting preliminary risk assessments of the numerous airborne toxic chemicals and their effects on vegetation and would provide research guidance.

- Quantify and model the exposure, deposition velocity, and absorption of air toxics to plants.

- Determine the biochemical and physiological responses of plants to chronic exposures to air toxic chemicals and develop exposure-response functions. This research then could be extended to quantify the response of plant populations and simulated plant communities.

- Initiate long-term studies to determine sensitive elements of plant community structure and function that would lead to significant change and degradation from air toxic exposure. This research would identify unacceptable change in plant communities and identify early warning signals.

ORGANOCHLORINES AND POLYCYCLIC AROMATIC COMPOUNDS IN THE HIGH ARCTIC

G.W. Patton[1] and T.F. Bidleman[2]

[1]Environmental Science Dept., Battelle - Pacific Northwest Laboratory, Richland, WA
[2]Dept. of Chemistry and Marine Science Program, University of South Carolina, Columbia, SC

INTRODUCTION

The Arctic is one of the most remote and isolated areas in the world. Despite the region's seemingly pristine character, polar ecosystems are polluted by anthropogenic emissions from temperate latitudes. Organochlorine (OC) pesticides and polychlorinated biphenyls (PCBs) have been well documented in the biota of the region (Bowes and Jonkel, 1975; Addison and Zinck, 1986; Norstrom and Muir, 1988). The harsh polar environment requires that marine animals store large amounts of fats, thus enabling them to accumulate high levels of lipophilic OC compounds. Native people still rely heavily on marine animals for their food. A recent study reported the insecticide toxaphene (polychlorinated camphenes, PCCs) in fish from inland lakes of the Northwest Territories, Canada (Muir et al., 1990). Long range atmospheric transport appears to be a major pathway of OC pesticides and PCBs into the Arctic. Several studies have demonstrated or suggested that aerial concentrations of these compounds can be linked to marine ecosystems (Norstrom and Muir, 1988; Muir et al., 1990; Patton et al., 1989; Hargrave et al., 1988; Bidleman et al., 1989). A better understanding of the concentrations, sources, and fate of organic contaminants in this region is needed.

The polar atmosphere is a unique place to study air transport of organic compounds, due to the large seasonal differences in temperature, photoperiod, and particulate loadings. Most of the pollution studies have centered around the arctic haze aerosol. Eastern Europe and Asia are the most likely sources of the haze, which is composed largely of sulfate, elemental carbon, and other combustion products. The haze pollution is seasonal with a maximum in the winter-early spring and a minimum in the late summer-fall (Barrie, 1986).

There is a limited but growing body of information on the types and levels of OC pesticides and PCBs in arctic air. Tanabe and Tatsukawa (1980) measured DDT and hexachlorocyclohexanes (HCHs) over the Bering Sea. Workers from the Norwegian Institute for Air Research (Oehme and Stray, 1982; Oehme and Ottar, 1984; Pacyna and Oehme, 1988) investigated concentrations and temporal changes in PCBs, HCHs, chlordane, and heavy chlorobenzenes in air over Spitzbergen, Bear Island, and Jan Mayan. Hoff and Chan (1986) measured chlordane isomers in the atmosphere over Mould Bay, Northwest Territories, Canada. The research group (Patton et al., 1989; Bidleman et al., 1989) used a floating ice island in the Beaufort Sea as a platform to collect HCHs, hexachlorobenzene (HCB), chlordanes, the DDT group, PCBs, and PCCs in arctic summer air. Hargrave et al. (1988) also measured OC levels in air, water, snow, sediments, and biota at the ice island.

Very little information exists on the types and levels of polycyclic aromatic hydrocarbons (PAHs) in the Arctic. Daisey et al. (1981) measured PAHs in spring and summer air in Barrow, AK, and spring air at Narwahl Island. Fluoranthene (FLA) has been reported in the atmosphere of the Norwegian Arctic (Pacyna and Oehme, 1988). PAHs and arctic haze emanate from combustion sources and should be correlated. However this has not yet been established.

The Canadian Government maintains a joint weather station and military base at Alert, on the northeastern shore of Ellesmere Island [(82.5 N, 62.3 W (Figure 1)]. We collected high volume air samples at Alert during February - April 1988 to determine the types and level of OC chemicals and PAH in Arctic winter air.

METHODS

Air volumes of 2050 to 2490 m^3 were pulled through two glass fiber filters (GFF) and two polyurethane foam (PUF) plugs at flow rates of 0.5 to 0.6 m^3/min using high volume pumps (Billings and Bidleman, 1983). Collections were made on an elevated plateau about 150 m above the base, approximately 5.5 km from the base. Electrical power for the pumps was supplied from the base's generator. Contamination from the generator plume should have been minimal due to the prevailing downward flow of air from the sampling hill to the station and a tight inversion layer over the camp during periods of calm wind. Determining the extent of contamination from the base was not

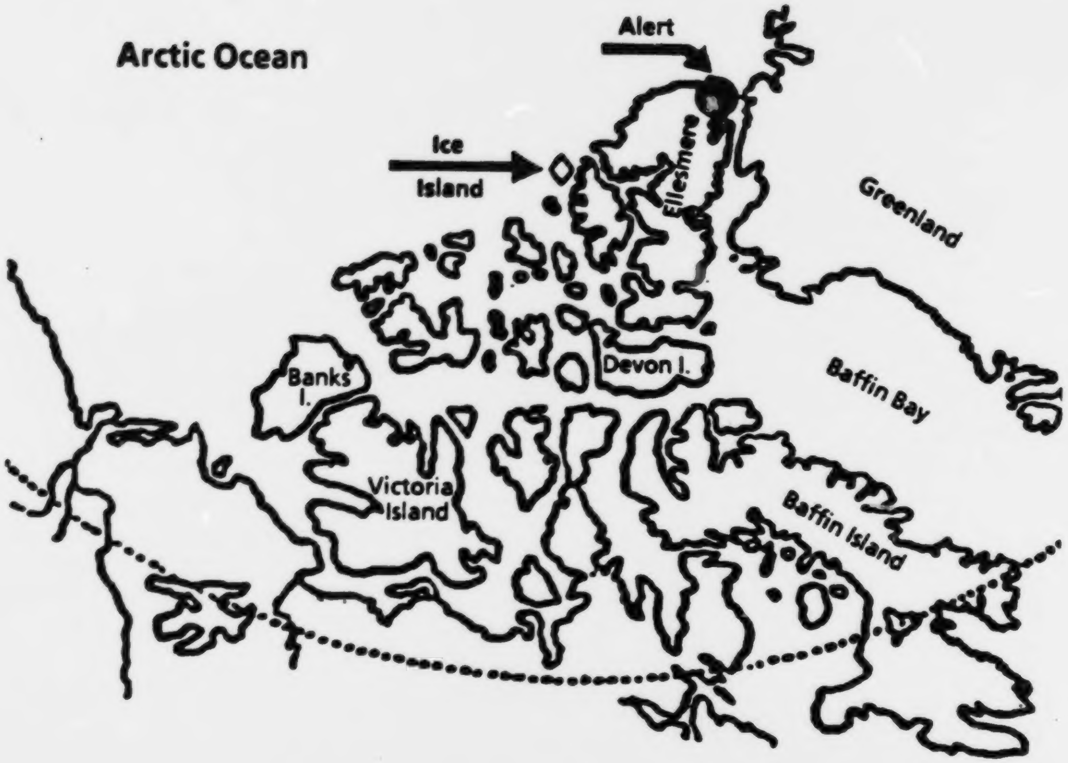
Arctic Ocean
Alert
Ice
Island
Ellesmere
Greenland
Banks
I.
Devon I.
Baffin Bay
Victoria
Island
Baffin Island

FIGURE 1. Location of Alert, Northwest Territories, Canada, and the Ice Island during August 1986 to June 1987 (Patton et al., 1989).

practical during this experiment. Temperatures and daylight hours during the sampling period ranged between -17 to -42°C and 0 to 24 h, respectively.

PUF plugs were extracted in a Soxhlet apparatus with petroleum ether, and GFF were refluxed with dichloromethane. Sample extracts were concentrated into isooctane and analyzed for dibenzofuran (DBF) and biphenyl by capillary gas chromatography - mass spectroscopy (GC-MS) using electron impact ionization (EI) and selected ion monitoring (SIM). DBF and biphenyl were quantified against external standards. The extracts were then cleaned up and fractionated using alumina-silicic acid column chromatography following the methods of Billings and Bidleman (1983). PAHs were analyzed by capillary GC-MS using EI and SIM. The PAHs were quantified using deuterated internal standards. The extracts were then treated with 18 M sulfuric acid and analyzed for OC and PCBs using capillary GC with electron capture detection (ECD). Pesticides and PCBs were quantified by external standards. PCCs were analyzed by GC-negative ion-MS (GC-NIMS); ions monitored were 309, 311, 343, 345, 379, 381, 413 and 415.

The low temperatures during the sampling period allowed the GFF-PUF system to retain compounds as volatile as pentachlorobenzene (PeCB) and biphenyl with very low breakthrough to the back PUF. The more volatile 1,2,4,5-tetrachlorobenzene was found in equal amounts in both PUF traps and thus no quantitative results could be obtained. Recoveries of PeCB, HCHs, HCB, fluorene (FLE), phenanthrene (PH), DBF, and biphenyl averaged 75% and results were corrected for this yield. Recovery of all other compounds was 80 to 115% and no corrections were made.

ORGANOCHLORINE RESULTS

Concentrations of gaseous + particulate chlorobenzenes and OC pesticides are given in Table 1 and a comparison of our results to those of others is presented in Table 2. PeCB, HCB, α-HCH, and γ-HCH were found in all samples. Pentachlorobenzene and HCB levels are similar to other values reported in the northern hemisphere (Bidleman et al., 1987). Compared to the ice-island study, the level of α-HCH was decreased by a factor of 2, while γ-HCH was fairly constant for both trips. Beta-HCH was found in 4 of 5 samples at concentrations an order of magnitude lower than γ-HCH.

HCH insecticides are applied as either a technical mixture (55 to 80% α-HCH, 5 to 14% γ-HCH, 8 to 15% β-HCH) (Metcalf, 1955), or as pure γ-HCH (lindane). In North America and Europe pure γ-HCH is used, whereas Asia, the Middle East, and Mexico use the technical mixture (FAOUN, 1978-1986). Tanabe et al. (1982) suggested that the heavy use of technical HCH by countries in the eastern hemisphere is responsible for the predominance of α-HCH. For this study, the α-HCH:γ-HCH

TABLE 1. AIRBORNE ORGANOCHLORINES AT ALERT, CANADA (1988)[a]

	(pg/m^3)				
Sample #	PV 4	PV 5	PV 12	PV 14	PV 15
Dates	2/28-3/2	3/2-3/5	3/23-3/26	3/29-4/1	4/1-4/4
Volume,m^3	2050	2175	2300	2461	2490
PeCB[e]	41	49	63	24	85
HCB	100	140	130	120	130
α-HCH	100	140	270	150	130
β-HCH	-[b]	1.6	1.3	1.8	1.6
γ-HCH	20	17	31	31	15
heptacl	0.33	0.84	0.22	-	-
heptaex	1.0	1.6	1.5	0.39	0.33
TC	0.69	2.2	1.3	0.74	0.78
CC	0.78	2.5	1.3	0.85	0.73
TN	0.50	2.0	1.1	0.70	0.59
p,p' -DDE	0.64	1.2	0.91	1.1	0.54
p,p' -DDT	-	2.3	1.7	1.8	1.0
PCB[c]	31	-	34	60	29
PCC[d]	14	-	71	-	20

[a] Particulate + vapor phase.

[b] No data available.

[c] PCB were calculated as the sum of individual congeners.

[d] PCC concentrations are from GC-negative ion-MS.

[e] PeCB = pentachlorobenzene, HCB = hexachlorobenzene, HCH = hexachlorocyclohexane, heptacl = heptachlor, heptaex = heptachlor epoxide, TC = *trans*-chlordane, CC = *cis* -chlordane, TN = *trans*-nonachlor, PCB = polychlorinated biphenyls, PCC = polychlorinated camphenes (toxaphene).

ratio (α:γ) range was 4.8 to 8.7 with a mean ratio of 7.1. The α:γ ratio did not appear to vary with photoperiod. Researchers in the Norwegian Arctic (Oehme and Ottar, 1984; Pacyna and Oehme, 1988) found that α:γ ratios were lower in the winter-spring compared to summer-fall and suggested that the proportion of α-HCH is higher in older air masses due to the photochemical conversion of γ-HCH to α-HCH. The lack of a trend in the α:γ ratio we observed does not rule out the photochemical conversion hypothesis, which is based on winter time input of HCH and a stagnant (non-input) summer period when the conversion occurs. The sampling period was early enough that "fresh" input of HCHs could still be occurring and this would tend to suppress any trend in the α:γ

TABLE 2. COMPARISON OF MEAN REPORTED ORGANOCHLORINE LEVELS IN CANADIAN ARCTIC AIR

	(pg/m^3)					
	Alert This Work	ICE IS. USC(1)[a]	ICE IS. USC(1)[a]	ICE IS. BIO(2)[a]	ICE IS. BIO(2)[a]	Mould Bay(3)[a]
Dates	Feb-Apr. 1988	Sept. 1986	June 1987	May 1986	Sept. 1986	June 1984
HCB	120	189	>147	73	63	-[d]
α-HCH	160	546	340	425	253	-
γ-HCH	23	31	45	70	17	-
TC	1.1	1.1	2.3	-	-	0.96
CC	1.2	2.8	4.0	-	-	1.5
TN	0.99	1.5	3.7	-	-	1.3
ΣChlordane	3.3	5.4	10	3.6	1.9	3.8
ΣDDT	2.6	1.0	5.2	<1	<1	-
PCB[b]	38	15.1	17.6	-	-	-
PCC[c]	35	44	36	-	-	-

[a] References: (1) Patton et al., 1989.
(2) Hargrave et al., 1988.
(3) Hoff and Chan, 1986.

[b] PCB calculated as the sum of individual congeners.

[c] PCC calculated as toxaphene (from GC-MS data).

[d] No data available.

ratio. Also, the sampling period only extended five weeks into the light season (polar sunrise at Alert occurred on March 5, 1988) and there may not have been sufficient time for the photochemical conversion to occur.

Concentrations of *trans*-chlordane (TC), *cis*-chlordane (CC) and *trans*-nonachlor (TN) are given in Table 1. The overall concentrations of the chlordanes are lower than previously reported summer air concentrations in the Canadian Arctic (Table 2). The mean TC:CC ratio was 0.95 and no trend in this ratio with photoperiod was evident. Chlordanes are applied as a technical mixture. Trans-chlordane would be thought to predominate in air because it is the most abundant and volatile isomer in the technical mixture. Using Raoult's law and the isomer composition of the mixture, the predicted ratio of TC:CC in air is 1.7. Figure 2 compares TC:CC ratios for several locations and the ratio appears to decrease away from application areas (e.g., Columbia, SC). The TC:CC ratio for this winter study was twice as high as our previous value for arctic summer air.

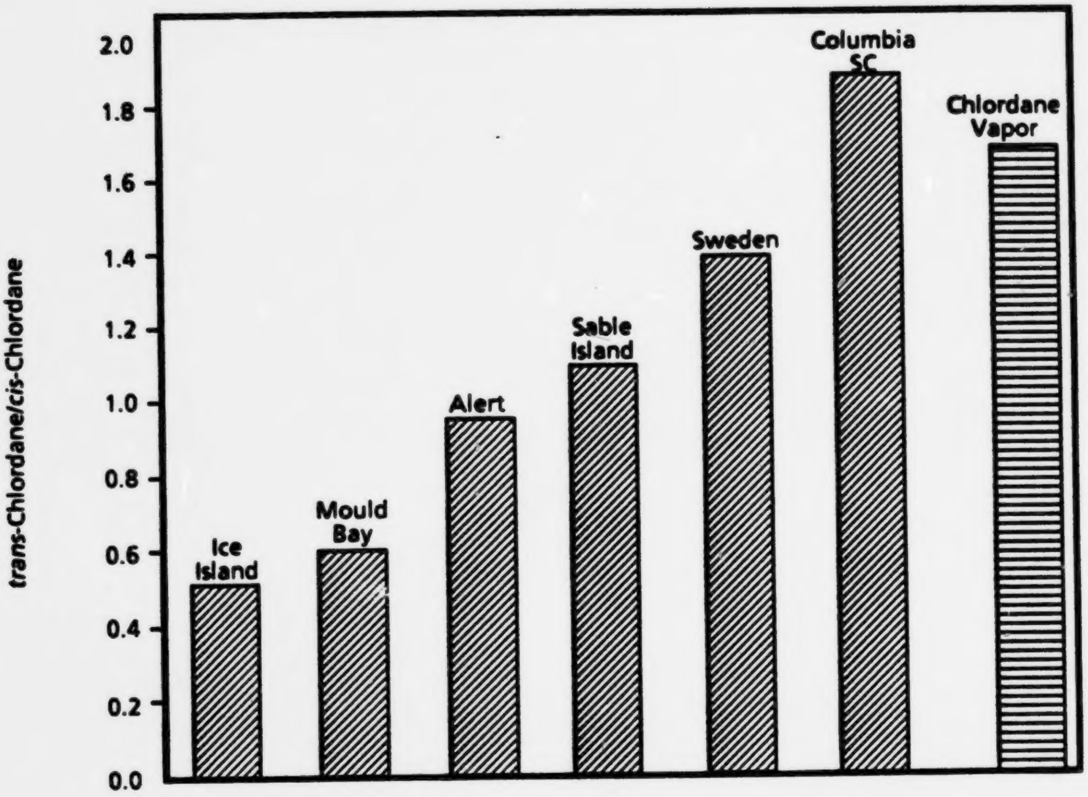

FIGURE 2. Comparison of *trans*-chlordane to *cis*-chlordane (TC:CC) ratios in air. Sources: Ice Island (Patton et al., 1989); Mould Bay (Hoff and Chan, 1986); Alert (this work); Sable Island (Bidleman and Addision, unpublished data); Sweden (Bidleman et al., 1987); Columbia, SC (Forman and Bidleman, 1987).

Bidleman et al. (1990) suggested that TC:CC ratios may be altered by selective degradation/removal of TC, and these ratios may provide clues to the transit time of OC in the atmosphere. The higher winter time TC:CC ratio (relative to summer) may indicate new or continuing input of chlordane into the arctic atmosphere during this period, while the lower summer ratio may indicate a stagnant (non-input) period for the arctic summer where selective degradation/removal could occur.

The levels of *p,p'*-DDT and *p,p'*-DDE in Alert air are given in Table 1. Concentrations of *p,p'*-DDT were roughly double the *p,p'*-DDE levels in all of the samples. With GC-ECD results there is a possibility that DDT levels were inflated by coeluting PCC congeners. The presence of *p,p'*-DDT in the samples was confirmed by several GC-MS methods (GC-NIMS and GC-high resolution-MS); however, quantification of the GC-MS results was not attempted and the GC-ECD values for *p,p'*-DDT and *p,p'*-DDE should be taken as upper limits. Other DDT-group compounds found by both GC-ECD and GC-MS were *o,p'*-DDT and *p,p'*-DDD. Levels of *p,p'*-DDT and *p,p'*-DDE were similar to those found during the last part of the June 1987 Ice Island study (Table 2).

Levels of PCBs in Alert air are presented in Table 1. PCBs were calculated as the sum of individual congeners. The mean PCB concentration was 38 pg/m^3, about twice as high as the Ice Island result (Table 2). The more volatile PCBs dominated the congener distribution.

Concentrations of PCCs for three samples (calculated from GC-NIMS data) are given in Table 1. The mean PCC level was 35 pg/m^3, similar to the mean concentration (44 pg/m^3) from the Ice-Island study (Patton et al., 1989). The more volatile PCCs (6-7 chlorinated camphenes) were more abundant in the samples than the heavier PCCs (8-9 chlorinated camphenes). Of the OC pesticides identified in Alert air, PCCs were second in abundance (after HCHs) which may explain the high concentrations of PCCs in fish from Northwest Terretories, Canada (Muir et al., 1990).

POLYCYCLIC AROMATIC COMPOUND RESULTS

Concentrations of PAHs and biphenyl in Alert air are given in Table 3. DBF was found in all samples (DBF was not determined in PV#12) and was present almost exclusively in the vapor phase. The mean DBF level was seven times larger than the value reported for North Pacific air (Atlas and Giam, 1989). Biphenyl was also found in the vapor phase of all samples at an average level of 1250 pg/m^3 (Tables 3 and 4). Full scan mass spectra of DBF and biphenyl from a sample extract are shown in Figure 3.

A comparison of the PAH levels to those of other researchers is given in Table 4. The winter concentrations were well below levels reported for winter air at Barrow, AK, and were more similar

TABLE 3. AIRBORNE POLYCYCLIC AROMATIC COMPOUNDS AT ALERT, NORTHWEST TERRETORIES, CANADA (1988)

	(pg/m^3)				
Sample #	PV 4	PV 5	PV 12	PV 14	PV 15
DBF[a]	1600	870	-[b]	2800	1700
Biph	1250	580	670	1400	700
FLE	110	200	440	340	100
PH	6.6	26	130	120	34
AN	-	-	-	0.78	0.47
2-m-PH	0.16	3.2	-	2.9	0.76
FLA	7.7	12	74	74	30
PY	3.0	1.9	50	49	14
B(a)A	-	0.75	8.3	3.0	3.6
CR	4.0	5.8	24	21	11
B(b)F	6.4	8.0	23	19	17
B(k)F	-	-	13	-	-
B(e)P	1.8	2.0	8.0	5.6	4.0
B(a)P	1.0	-	3.1	3.4	3.2
I(cd)P	2.0	-	5.5	5.6	4.1
B(ghi)P	1.7	1.2	8.6	3.6	4.5

[a] DBF = dibenzofuran, Biph = biphenyl, FLE = fluorene, PH = phenanthrene, AN = anthracene, 2-m-PH = 2-methyl-phenanthrene, FLA = fluoranthene, PY = pyrene, B*[a]*A = benzo*(a)*anthracene, CR = chrysene, B[b]F = benzo*(b)*fluoranthene, B[k]F = benzo*(k)*fluoranthene, B[e]P = benzo*(e)*pyrene, B[a]P = benzo*(a)*pyrene, I*(cd)*P = Indeno(1,2,3-cd)pyrene, B*(ghi)*P = benzo(ghi)perylene.

[b] No data available.

to levels reported for April at Narwahl Island (off the northern shore of Alaska) and summer air at Barrow (Daisey et al., 1981). PAH levels at Alert were higher than those reported in the North Pacific (Atlas and Giam, 1989). The low temperatures and higher particle loads at Alert dramatically raised the particle:vapor ratios relative to the ratios reported in warmer North Pacific air (Table 4).

PAH in the volatility range between FLE to benzo*[ghi]* perylene (B*[ghi]* P) are presented in Tables 3 and 4. FLE was found exclusively in the vapor phase at a mean level of 240 pg/m^3. Phenanthrene (PH), FLA, pyrene (PY) and chrysene (CR) were found both in the gas and particulate phases. The amount of these compounds in the particulate phase was operationally defined (front GFF - back GFF) and the vapor phase was defined as ((2 x (back GFF) + PUF)).

TABLE 4. COMPARISON OF MEAN SELECTED GAS-PHASE AND PARTICULATE POLYCYCLIC AROMATIC COMPOUNDS IN REMOTE ATMOSPHERES

	(pg/m^3)						
	Alert (This Work)		North Pacific (1)[a]		Alaska (2)[a]		
					Barrow		Narwahl I.
					Particulate Only		
Compound	Gas	Part.	Gas	Part.	(Aug.)	(Mar.)	(April)
DBF	1700	-[b]	248	-	-	-	-
Biph	920	-	-	-	-	-	-
FLE	240	-	16	0.1	-	-	-
PH	23	40	14	2.2	17	120	20
FLA	5	35	2.0	1.3	28	290	60
PY	3	21	3.0	1.1	29	310	150
CR	1	12	1.0	1.8	5	80	-
Benzofluoranthenes	-	28	-	2.1	-	-	-
B*[a]* P	-	2.7	-	0.4	10	30	-
B*[e]* P	-	4.3	-	1.0	-	210	-
B*[ghi]* P	-	3.9	-	1.0	10	70	-
I*[cd]* P	-	4.3	-	0.7	-	-	-

[a] References: (1) Atlas and Giam, 1989.
(2) Daisey et al., 1981.

[b] No data available.

These corrections were made in an attempt to correct for gas adsorption to the GFF matrix (Ligocki and Pankow, 1989). For the PAHs with vapor pressures below CR, the compounds were found entirely on the front GFF.

CONCLUSION

The finding of OC and PAHs in arctic winter air provides additional evidence for the long-range, atmospheric transport of anthropogenic pollutants to polar regions. In general, these chemicals are persistent and toxic. The OC have bioaccumulation potential. Despite low atmospheric concentrations, these pollutants impact the arctic environment and high levels can accumulate in polar food webs. This study has provided the first measurement of both particulate and vapor phase PAH

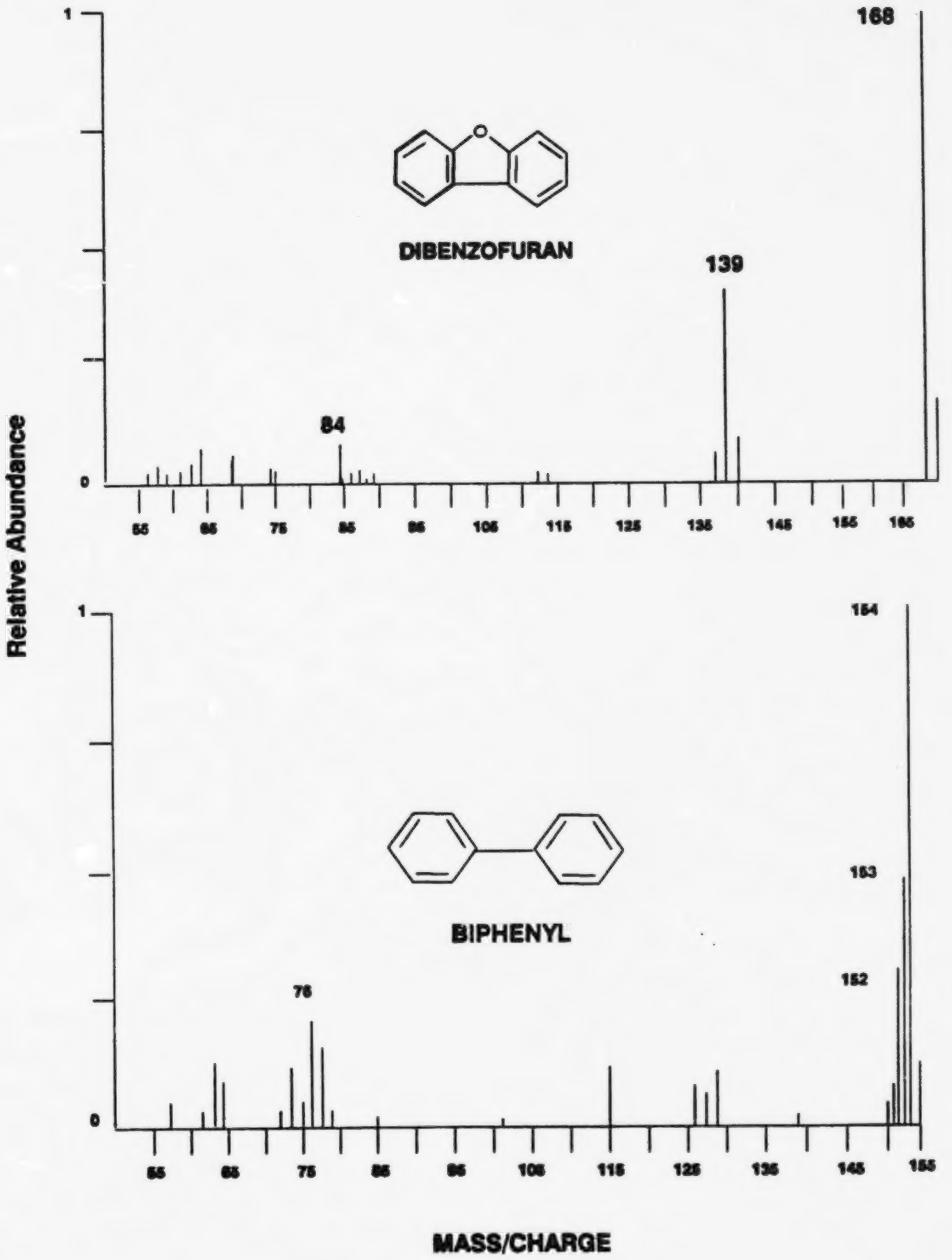

FIGURE 3. Full scan mass spectrum of the dibenzofuran and biphenyl peaks from an Alert air sample.

in the Canadian Arctic. Despite the extreme cold, some PAHs have a sizable vapor phase component.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation, Division of Atmospheric Chemistry. Thanks to L. Barrie of Atmospheric Environment Service, Downsview, Canada, for extending the invitation for us to participate in the Polar Sunrise Experiment and for providing travel and salary support. GC-MS analysis of toxaphene and DDT-group compounds were provided by M.D. Walla and W.E. Cotham, Jr. A special thanks goes to the many people at the Alert weather station and the "Frozen Chosen" at C.F.S., Alert, who helped make this research possible.

AIR-SEA EXCHANGE OF HEXACHLOROCYCLOHEXANE IN THE BERING AND CHUKCHI SEAS

Daniel A. Hinckley[1], Terry F. Bidleman[2], and Clifford P. Rice[3]

[1] Ebasco Environmental, Bellevue, WA
[2] Dept. of Chemistry and Marine Science Program, University of South Carolina, Columbia, SC
[3] U.S. Fish and Wildlife Research Center, Laurel, MD

INTRODUCTION

Recent evidence documents long-range atmospheric transport and subsequent deposition of organochlorine contaminants to terrestrial and aquatic ecosystems (Pacyna and Oehme, 1988; Hargrave et al., 1988; Patton et al., 1989; Gregor and Gummer, 1989). As a result, these contaminants have been found in arctic fish, marine mammals, birds, and plankton (Norstrom et al., 1988; Muir et al., 1988). This raises concern because the food chain in these cold, remote locations is relatively simple and may lead to high concentrations of pollutants in the diet of native Inuit (Muir et al., in press; DeWailly et al., 1989).

The third American-Soviet joint expedition to the Bering and Chukchi Seas in 1988 took place on the R/V Akademik Korolev. This was the 47th oceanographic cruise for the Akademik Korolev and the cruise was commonly termed the AK-47. The primary goal of the AK-47 was to characterize the ecology of these waters. The Soviet Union and United States share a border between territorial waters in this region and, as a result, most scientific studies have been on either the Soviet or American side. This study was co-sponsored by the U.S. Department of Interior and the U.S.S.R. Academy of Science. Therefore, the joint sponsorship allowed the first complete environmental survey of the area. Several research groups consisting of Soviet and American scientists were established to investigate the ecology of the Bering and Chukchi Seas among other things. This paper will focus on the air-sea exchange of hexachlorocyclohexane (HCH).

The insecticide HCH is used throughout the world and is available in two formulations, technical-HCH and lindane. Technical-HCH is a mixture of five isomers in the following proportions (Metcalf, 1955): (1) α, 55 to 80%, (2) β, 5 to 14%, (3) γ, 8 to 15%, (4) δ, 2 to 16%, and (5) ε, 3 to 5%. Although all isomers are toxic, only the gamma isomer is insecticidal and it is produced in pure form as the insecticide lindane. Technical-HCH is now banned in the United States, the Soviet Union, and western Europe, but continues to be heavily used in Asia. Limited data are available about the usage of HCH. Tanabe et al. (1982) reported the use of 77,000 metric tons of technical-HCH in India from 1975 to 1978 and the production of 20,000 metric tons/year in one plant in China. The Food and Agricultural Organization (FAO) Production Yearbook (1986-87), shows 23,400 metric tons/year technical-HCH used in India between 1980 and 1985. Lindane usage has been reported as 1,440 metric tons/year in Italy from 1980 to 1984 (FAO Production Yearbook, 1986-87), and 29 metric tons/year in Scandinavian countries (Pacyna and Oehme, 1988). Together, the HCH isomers are the most abundant of the heavy organochlorines in the northern troposphere and surface waters. Because of their high concentrations, low volumes of air (15 to 20 m^3) and water (2 to 4 L) can be sampled and analyzed for levels of α-HCH and γ-HCH.

The deposition of organic compounds from the atmosphere is controlled by their physical properties (Bidleman, 1988). HCH physical properties behave differently from most other organochlorine pollutants. Vapor pressures and water solubilities of HCHs are sufficiently high that they remain primarily as gases in the atmosphere or dissolved in the water column with relatively small fractions sorbed onto particles. The exchange of HCH between the atmosphere and water depends on the concentration gradient at their interface and its Henry's Law constant. HCH has a low Henry's Law constant, facilitating transport from the atmosphere into water. A knowledge of air and surface water HCH concentrations, along with the appropriate Henry's Law constant, allows the determination of the equilibrium state for HCH in the water.

Consequently, surface (2 m) water concentrations of α-HCH and γ-HCH were determined at 19 stations of the AK-47 cruise, and air concentrations were measured at 16 of these same stations. Henry's Law was applied to atmospheric HCH levels and the equilibrium between the atmosphere and surface water was evaluated. In addition, HCH concentrations in the microlayer (top 200 μm), surface water (2 m), and 1000 m seawater were compared for two of these stations.

EXPERIMENTAL METHODS

Cruise Track

The cruise originated and terminated at the deep water port of Dutch Harbor, AK, and lasted from July 26 to September 2, 1988. The cruise track, shown in Figure 1, was a convoluted route in the Gulf of Anadyr, Southern Chukchi Sea, and Chirikov Basin. This is a shelf region with a maximum depth of about 80 m. Two polygons were sampled in the southern Bering Sea where depths up to 4000 m were encountered (Figure 1). Sampling duration at each oceanographic station was relatively short, lasting from 0.5 to 2 h. At these stations a specific conductivity/temperature/depth (CTD) probe was sent to the bottom for water column analysis, and nutrient and primary productivity studies were conducted. Sampling at each ecological station took place over 3 to 12 hours. In addition to CTD, nutrient and primary productivity measurements and water samples were taken throughout the water column for the determination of pollutant levels; and sediment, bacterial, phytoplankton, zooplankton, and benthic investigations were performed.

Sample Collection

Surface and deep water was collected using a variety of methods. Niskin and Go-Flo bottles were sent to the required depth on hydrowire or Kevlar line and triggered by sending a messenger down the wire. In addition, a water sampler, based on a design by Keizer et al. (1977), was constructed using two solvent bottles mounted on a wooden frame. Teflon elbows were cemented into the bottle caps, with a glass tube connecting the two bottles through the elbows. The "messenger" sent down the wire broke the glass tube, which allowed water to fill the solvent bottles. This sampler was used to collect surface water from 2 to 10 m and the bottles filled within 5 min. Microlayer water samples were collected at three stations from a small boat at least 1 km from the ship using a stainless steel screen technique (Garrett, 1965).

Air was pulled through two or three polyurethane foam (PUF) plugs (4.8 cm diameter, 3.2 cm thickness) in a clean thick-walled glass tube (4.0 cm ID, 15 cm length) using a brushless pressure-vacuum pump (Millipore Corp., Milford, MA). Air was sampled continuously for 8 to 24 h at a flow rate of 20 L/min, which yielded volumes of 10 to 30 m^3. Flow rates were determined using an in-line Top-Trak Model 820 flow monitor (Sierra Instruments, Atlanta, GA). Breakthrough of analytes from front to back PUF plugs was monitored by the separate analysis of each plug. Because of the low air volumes sampled, only α-HCH, γ-HCH and hexachlorobenzene (HCB) were quantified.

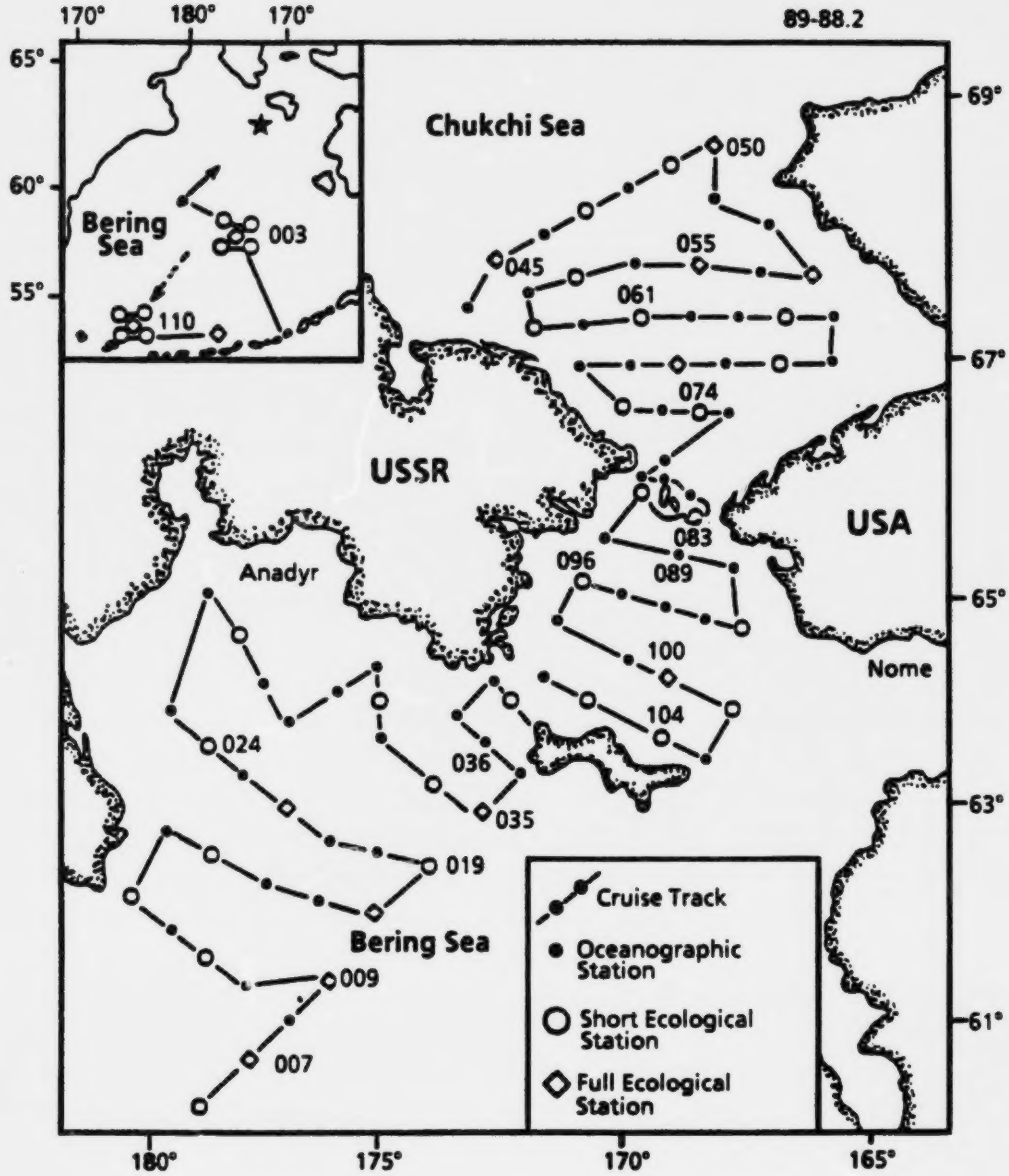
89-88.2
170°
180°
170°
65°
60°
55°
Bering Sea
003
110
Chukchi Sea
050
055
045
061
074
USSR
USA
083
096
089
Anadyr
100
Nome
104
036
035
024
019
Bering Sea
009
007
Cruise Track
Oceanographic Station
Short Ecological Station
Full Ecological Station
69°
67°
65°
63°
61°
180°
175°
170°
165°

FIGURE 1. Cruise track of the AK-47, July 26, 1988 to September 2, 1988. The three digit numbers indicate stations.

Preconcentration and Cleanup

Analytes from 3.5 L water were preconcentrated by two methods: (1) liquid-liquid extraction into 300 ml methylene chloride, and (2) adsorption onto C_8 bonded-phase cartridges (Hinckley and Bidleman, 1989). The methylene chloride extract was reduced in volume using a rotary evaporator and the solvent was replaced with pesticide-quality hexane prior to gas chromatographic (GC) analysis. The C_8 bonded-phase cartridges were eluted with 3 ml 1:1 ethyl ether-hexane, and blown down into pure hexane with nitrogen. Polyurethane foam plugs were extracted for 6 h in a Soxhlet apparatus with petroleum ether, the petroleum ether volume was reduced using the rotary evaporator, and the solvent was replaced with hexane or isooctane prior to GC analysis. All extracts were treated with concentrated sulfuric acid for cleanup.

Gas Chromatographic Analysis

Gas chromatographic analyses were conducted using a Hewlett Packard (HP) 5840, Varian 3700, or Carlo Erba 4160 chromatograph with ^{63}Ni electron capture detectors (GC-ECD). The instruments contained 25-m bonded-phase fused silica columns (polydimethylsiloxane, 5% phenyl, Hewlett Packard or SGE Corp.). Carrier gases were hydrogen or helium at 30 to 40 cm/s, the injector temperature was 240℃ and the detector was 320℃. Samples were injected using a splitless Grob technique. Chromatographic data were collected using the HP-5840 integrator, an HP-3390A, or a Shimadzu Chromatopac CR3A integrator. Alpha-HCH and γ-HCH were confirmed by GC-electron impact mass spectrometry (GC-MS) with selected monitoring of the 181 and 217 ions using an HP 5890 GC with a mass selective detector and the same type of column used for GC-ECD work.

Henry's Law Constant Determination

Air-sea exchange is controlled by Henry's Law:

$$C_g = K_H \times C_1 \tag{1}$$

where C_g and C_1 are equilibrium concentrations in the air and surface water, respectively, and K_H is the distribution coefficient. K_H can be further defined:

$$K_H = H/RT \tag{2}$$

where H is the Henry's Law constant (atm-m^3/mol), R is the gas constant

(8.2×10^{-5} m^3-atm/mol-K), and T the surface water temperature (K). Lastly, the Henry's Law constant, H, can be thermodynamically defined as:

$$H = p^\circ / c^\circ \tag{3}$$

where p° is the vapor pressure and c° the aqueous solubility of the compound. Use of Equation 3 allows calculation of H; however, the aqueous solubilities of HCHs are not well characterized as a function of temperature and we opted for direct determination of H in the laboratory.

Henry's Law constants have been determined in the laboratory by the gas stripping method (Mackay et al., 1979). In this technique an aqueous solution of the HCHs in a thermostat-controlled vessel is purged with air to strip the HCH vapors. The equation for the loss of HCH from solution with the time is

$$\ln (C_t/C_o) = -(HG/VRT)t \tag{4}$$

where C_t and C_o are the aqueous HCH concentrations at time = t and at time = 0, G is the gas flow rate (m^3/h), and V is the solution volume (m^3). The H value is determined by the regression of (C_t/C_o) on t (h) which has a slope of -(HG/VRT) (Mackay et al., 1979).

Henry's Law constants were determined at 23°C (n=3) using artificial seawater (Horne, 1969). The seawater was stripped with a cleaned air stream for 95 to 120 h. The gas-stream flow (350 L/min) was monitored daily using a bubble flow-meter. Daily water samples were taken for analysis of α-HCH and γ-HCH. Initial concentrations were approximately 6 μg/L for both analytes. After 120 h the concentration of α-HCH and γ-HCH reduced to 1 ug/L and 3ug/L, respectively. The state of equilibrium was monitored by varying the depth through which the bubbles rose. The Henry's Law constant determined at 25 cm depth was the same (within experimental error) as that found using 45 cm depth.

Quality Control

Spike recovery of 17 ng of α-HCH and γ-HCH, shown in Figure 2, ranged from 80% to 95%. HCH concentrations reported in this paper have not been corrected for recovery. Air sample breakthrough from front to back PUF averaged 32% and 18% for γ-HCH and α-HCH, respectively, and 12% for HCB. Limits of detection, based on the area of lowest observable peaks near the area of interest, were 0.15 ng/L in water and 0.03 ng/m^3 in air for both α-HCH and γ-HCH. Liquid-liquid

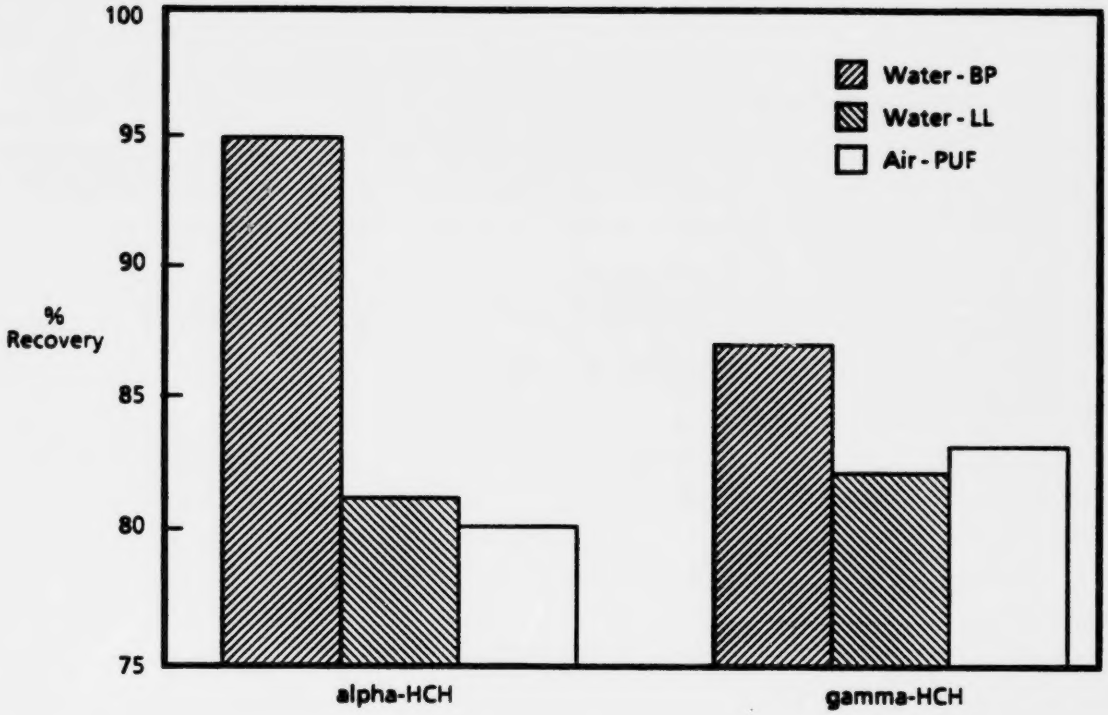

FIGURE 2. Spike recovery of 17 ng α-HCH and γ-HCH from bonded-phase cartridges (BP), liquid-liquid extraction (LL), and polyurethane foam plugs (PUF) obtained on the AK-47 cruise.

and C_8 cartridge methods of preconcentration were compared at four stations (003, 007, 009, and 019; Figure 1). As comparable levels of HCH were found, regardless of the preconcentration method, water at all remaining stations was analyzed using the liquid-liquid extraction method.

RESULTS

Water and Air Concentrations

Microlayer and surface water concentrations of α-HCH and γ-HCH for station 003 are shown in Table 1. No enhancement of HCH was found in the microlayer. There was a significant decrease in levels of HCH with depth at station 110. The decrease from 2 m to 1000 m for α-HCH and γ-HCH was 81% and 44%, respectively. These results are similar to those reported by Tanabe and Tatsukawa (1980) in the North Pacific. Transport of HCH from surface to deep water is hindered by low particle association of HCH (Tanabe and Tatsukawa, 1983). Consequently, HCH entering surface water from the atmosphere will tend to stay at the surface and not be removed to bottom water on particles, resulting in lower HCH concentrations in deep Bering Sea water.

TABLE 1. COMPARISON OF HCH[a] IN MICROLAYER, SURFACE, AND DEEP WATER

	Concentration of HCH (ng/L)					
Station	Microlayer		Surface (2 m)		Deep (1000 m)	
	α	γ	α	γ	α	γ
003	2.07	0.52	2.56	0.63	-[b]	-
110	-	-	2.25	0.43	0.23	0.24

[a] N=1

[b] No data available

Levels of α-HCH and γ-HCH in surface water (19 stations) and air (17 stations), and HCB in air are given in Table 2, and are compared with literature values in Table 3. HCH concentrations found during the AK-47 are similar to levels found by Kawano et al. (1988) in the Bering Sea. Beaufort Sea locations farther north appear to have higher HCH concentrations. Blanca Bay, Argentina, has been included in this table as an example of local estuarine contamination.

TABLE 2. SUMMARY OF AIR AND SURFACE WATER HCH CONCENTRATIONS

	Air (ng/m^3)	Water (ng/L)
α-HCH		
n	17	19
mean ± sd	0.21 ± 0.06	2.35 ± 0.36
range	0.12 - 0.34	1.78 - 2.92
γ-HCH		
n	17	19
mean ± sd	0.13 ± 0.05	0.52 ± 0.10
range	0.08 - 0.29	0.34 - 0.69
HCB		
n	17	-[a]
mean ± sd	0.17 ± 0.04	
range	0.12 - 0.27	

[a] No data available

TABLE 3. COMPARISON OF α-HCH AND γ-HCH CONCENTRATIONS IN AIR AND WATER FROM THIS STUDY WITH REPORTED VALUES

Location (Ref.)	Date	Water (ng/L)		Air (ng/m^3)	
		α-HCH	γ-HCH	α-HCH	γ-HCH
Bering and Chukchi Seas (this work)	8/88	2.35	0.52	0.20	0.13
N. Pacific and Bering Sea (Kawano et al., 1988)	7/81	2.75	0.65	-[b]	-
Bering Sea (Tanabe and Tatsukawa, 1980)	7/79	3.9[a]		-	-
Beaufort Sea (Hargrave et al., 1988)	6/86	4.40	0.57	0.45	0.07
Beaufort Sea (Patton et al., 1989)	6/87	7.1	0.81	0.34	0.05
Hudson Bay (McCrea and Fischer, 1986)	1980-81	6.42	0.86	-	-
Blanca Bay, Argentina (Sericano and Pucci, 1984)	1980-81	48.2	54.2	-	-

[a] Sum of α-HCH and γ-HCH.
[b] No data available.

An interesting aspect of the atmospheric HCH data is the α/γ ratio. This has been suggested as a marker for recent atmospheric transport of these pollutants (Pacyna and Oehme, 1988). During this cruise the α/γ ratio ranged from 1 to 3 and averaged 1.4. This is a much lower value than that found in the Canadian Arctic, and is actually lower than in most regions (Pacyna and Oehme, 1988). This may indicate recent atmospheric transport of lindane from the Soviet Union and Asia over the Bering and Chukchi Seas.

Henry's Law Constants and Air-Sea Exchange

The Henry's Law constants for α-HCH and γ-HCH in artificial seawater at 23℃, along with literature values, are shown in Table 4. Comparison of experimental and literature values is favorable, indicating the stripping system is at equilibrium. The Henry's Law constants at other temperatures have not yet been determined, and temperature dependence of H for the HCHs was assumed to be similar to that of PCBs (Patton et al., 1989; Burkhard et al., 1985). Station 061 in the Chukchi Sea, where the surface water was 5℃, had air concentrations of 0.19 ng/m^3 and 0.13 ng/m^3 for α-HCH and γ-HCH, respectively. Using $H = 1.24 \times 10^{-6}$ atm-m^3/mol for α-HCH and $H = 6.27 \times 10^{-5}$ atm-m^3/mol for γ-HCH at 5℃ and applying Equation 1, equilibrium surface water concentrations were calculated. The results reveal α-HCH in apparent equilibrium between the air and water, while γ-HCH exhibits a large disequilibrium, with lindane fluxing from atmosphere to surface water (Figure 3). This may imply that fresh lindane, coming from the Soviet Union and Asia, is a source of the pollutant into Bering and Chukchi Sea surface water.

TABLE 4. HENRY'S LAW CONSTANTS (atm-m^3/mol) FOR HCH IN SEAWATER

Isomer	Temp. (℃)	This Work[a]	Other Work[b]
α-HCH	23	$6.5 \pm 1.0 \times 10^{-6}$ (n=4)	1.1×10^{-5}
y-HCH	23	$3.3 \pm 0.9 \times 10^{-6}$ (n=4)	2.5×10^{-6} [c]

[a] Mean ± standard deviation.
[b] Atlas et al., 1982; Fendlinger and Glotfelty, 1988.
[c] Calculated from reported fresh water value, assuming a 25% decrease of solubility in seawater (Masterson and Lee, 1972).

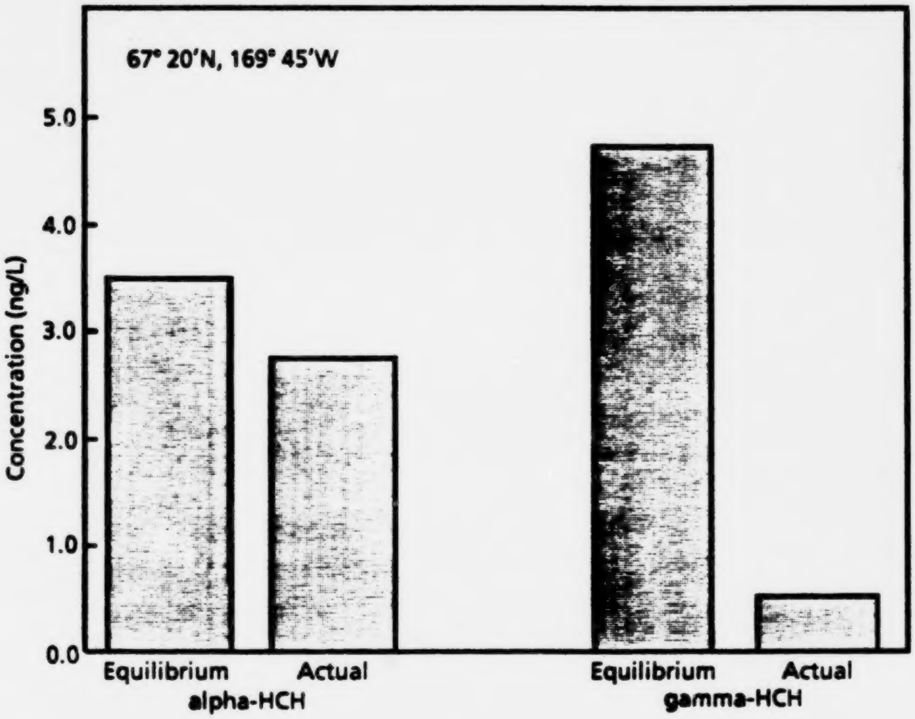

FIGURE 3. Comparison of surface water HCH concentrations in equilibrium with air (see text) with actual measured concentrations for station 061.

CONCLUSIONS

As a part of the 47th cruise of the R/V Akademik Korolev, cosponsored by the U.S. Department of Interior and the U.S.S.R. Academy of Science, air and surface water concentrations of α-HCH and γ-HCH have been determined for 16 locations in the Bering and Chukchi Seas. Concentrations of HCH were not enriched in microlayer water. Comparison of surface water (2 m) to deep water (1000 m) in the Bering Sea showed an 80% decrease in α-HCH and a 40% decrease in γ-HCH, indicative of an atmospheric source. Surface water concentrations were 2.35 ± 0.36 ng/L for α-HCH and 0.52 ± 0.10 ng/L for γ-HCH, similar to levels found by Kawano et al. (1988) in July 1981. Air concentrations were 0.21 ± 0.06 ng/m^3 and 0.13 ± 0.05 ng/m^3 for α-HCH and γ-HCH, respectively, and 0.17 ± 0.04 ng/m^3 for HCB. Levels of α-HCH and γ-HCH were similar to those found in the Canadian Arctic (Hargrave et al., 1988; Patton et al., 1989); however, γ-HCH concentrations in air were 2-4 times higher over the Bering and Chukchi Seas. Using Henry's Law constants determined in the laboratory and assuming temperature dependence of H similar to the PCBs, γ-HCH appears to be fluxing from the atmosphere to the ocean, whereas α-HCH in surface water appears to be in equilibrium with the atmosphere. This, along with higher α/γ air ratios than those usually found in the northern hemisphere, suggests recent atmospheric long-range transport of lindane from the Soviet Union and Asia to these waters.

Because of their relatively high water solubilities, bioconcentration factors (BCF) of the HCHs are lower than those of chlordanes and DDTs (Kawano et al., 1988). However the lower BCFs are offset by the much higher concentration of HCHs in seawater. As a result, concentrations of HCHs in fish and zooplankton from the Arctic are similar to or exceed those of PCBs and other organochlorine pesticides (Muir et al., 1988; Kawano et al., 1988).

ACKNOWLEDGMENTS

Special thanks to the U.S. Department of Interior, Fish and Wildlife Service, and the U.S.S.R. Academy of Sciences for sponsoring the 47th cruise of the R/V Akademik Korolev. The U.S. Environmental Protection Agency, Great Lakes Program Office, funded the laboratory Henry's Law constant determinations.

TRACE METAL DEPOSITION AND CYCLING IN FORESTED ECOSYSTEMS[1]

Andrew J. Friedland

Environmental Studies Program
Dartmouth College
Hanover, NH

INTRODUCTION

Trace metals are released into the atmosphere through a variety of human activities such as fossil fuel combustion, smelting, and manufacturing, as well as through natural processes such as volcanoes. Both short- and long-range atmospheric transport and deposition occur. Forests are one ecosystem where trace metals accumulate. The accumulation of trace metals in some forests, specifically in the organic-rich horizon of the soil, is well documented. The effects of trace metals on biological processes are not well understood. This report will discuss the evidence for trace metal deposition and accumulation in forests of the northeastern United States and the potential for adverse effects on forest processes.

STATEMENT OF THE PROBLEM

Concentrations and amounts of lead, and possibly copper, zinc, nickel and cadmium, in many forests are substantially higher today than they were earlier this century. The primary source of the lead and partially for other elements is air pollution. The effect that the accumulation of these trace metals have on nutrient cycling, trace metal cycling, soil biota diversity and abundance, decomposition processes, and plant root growth is not known.

---

[1] Portions of this report have appeared in the following publications: Friedland et al., 1984a,b; Friedland et al., 1986b; and Friedland, 1989.

EVIDENCE FOR ATMOSPHERIC TRANSPORT AND DEPOSITION OF TRACE METALS

Sources of Trace Metals in Forest Ecosystems

There are three major sources of trace metals in most terrestrial ecosystems: (1) the underlying parent material, (2) the atmosphere, and (3) the biosphere. Biotic sources of trace metals are originally obtained from one of the other two sources. In different systems, the relative input from each of these three sources varies.

Parent Material Inputs

In a natural, undisturbed ecosystem, the primary source of most trace metals is the underlying bedrock (Adriano, 1986) or surface material transported via the atmosphere from another location (Davidson et al., 1981). Except in areas of ore deposits and other unusually high concentrations of metals, the trace metal content in most parent material is quite low. The average or range of concentrations for lithospheric material and sedimentary rocks for six trace metals is shown in Table 1. Trace metals in soils usually are derived from the underlying parent material and are often similar to parent material concentrations. Organic, soil-metal concentrations are generally higher than the underlying mineral soil (Friedland et al., 1986a) (Table 1).

Bedrock is not necessarily always the parent material. In certain environments, glacial till or fluvial and other sediments can be transported hundreds and even thousands of kilometers to new locations. The subsequent soil that is formed will have a very different physicochemical characterization than adjacent areas not covered by the transported soil (Birkeland 1984).

Weathering is the process by which rocks are slowly broken down into the mineral content. The weathering processes that occur over time--both physical and chemical--lead to the breakup of bedrock or surface rock, and release of elements, including trace metals, into the environment. These metals then may enter rivers, streams, and other aquatic systems as well as terrestrial systems.

Atmospheric Inputs

Emissions of trace metals as particulates and gases from volcanoes, forest fires, crustal material, and continental dust have always been a natural input to soils and ecosystems (Davidson et al., 1981). It is possible that before industrialization the combustion of dung and wood by humans was a source of trace metal pollution (Davidson et al., 1985). During the last 5000 years, human-related emissions of trace metals have become increasingly important. In considering the relative contribution of natural and human sources, many investigators have ignored vapor deposition of trace metals because of a paucity of data. However, data are available on the deposition of atmospheric mercury vapor, for example, in specific geographic areas, and to a lesser extent for the

TABLE 1. AVERAGE OR RANGE OF TRACE METAL CONCENTRATIONS IN CRUSTAL MATERIAL AND SOILS FROM A VARIETY OF LOCATIONS IN THE WORLD[a].

Element	Lithosphere	Sedimentary Rocks	Soils	
			Mineral	Organic
Nickel	75	48	16	70
Copper	24	30	20	350
Cadmium	0.5	1.0	0.2	0.9
Zinc	70	20-97	50	66
Mercury	0.243	0.040-0.055	0.070	0.161
Iron	31.5	6.7-49	17	44

[a] All concentrations are in parts per million. Source: Adriano 1986; Nriagu 1979a,b, 1980a,b. Modified after Friedland (1989).

entire globe, but they are often excluded from global estimates of mercury cycling (Lindberg, 1987; Galloway et al., 1982; Lantzy and Mackenzie, 1979).

Galloway et al. (1982) combined vapor emissions data with the dust particulate emissions data of Lantzy and Mackenzie (1979) and determined the ratio of atmospheric emission from natural and human-related sources for a number of trace metals. As expected, aluminum has a very low anthropogenic-to-natural emission ratio (approximately 0.15). Continental dust is the greatest source of aluminum in the atmosphere; industrial processes and fossil fuel combustion contribute only slightly to atmospheric aluminum. In some global estimates the anthropogenic-to-natural emission ratio for mercury is almost as low as the value for aluminum. Lead has perhaps the highest anthropogenic-to-natural emission ratio (approximately 346); automobile emissions and smelting are the two major sources of technogenic lead in the atmosphere. In the past decade, as North America and some European countries have used less leaded gasoline, the importance of automobile emissions as a source of lead has decreased.

Ecosystems receive trace metals through wet (e.g., rain) and dry (e.g., particulate) deposition. The relative contribution of precipitation, cloud water, and dry deposition to a forest, and the effect of the forest canopy on throughfall chemistry vary depending on site factors including elevation, topography, and vegetation (Lovett et al., 1982; Lovett et al., 1985). In high-elevational forests, cloud water may be a significant source of trace metals (Lovett et al., 1982). The relative contribution of wet versus dry deposition also may influence the relative solubilities of metals. In general, trace metals are less soluble in dry than in wet deposition.

Biotic Inputs

Inputs to a system from existing vegetation occur in a number of ways: (1) inputs from above-ground biomass, (2) inputs from roots and other below-ground biomass, and (3) leaching and wash off from leaf surfaces. These inputs also are considered fluxes within the ecosystem and will be discussed in greater detail in the next section. The lead concentration of most vegetation is relatively low despite evidence that it is probably five-times higher than prior to industrialization (Shirahata et al., 1980). In forested sites under a variety of conditions in Europe and North America, the amounts of lead, cadmium, and nickel in vegetation are somewhat lower than the amounts of the same metals in soil (Smith and Siccama, 1981; Friedland and Johnson, 1985). Of course, near smelters, vegetation levels of most trace metals are quite high (Jackson and Watson, 1977).

It is generally accepted that soil and other environmental trace metal concentrations are substantially greater today than they were hundreds of years ago (Settle and Patterson, 1980). The most direct evidence of increased trace metal concentrations in this century is available from forest floor (the organic horizon overlying the mineral soil) samples collected at two points in time from the same locations in Vermont and Massachusetts (Siccama et al., 1980; Friedland et al., 1984a). These studies indicate that lead concentration has increased by as much as 40% in less than two decades. By examining buried, organic horizons at a northern hardwood forest in New Hampshire, Johnson et al. (1982) were able to approximate lead concentrations from earlier this century. They assumed that the buried organic horizons were sealed from the atmosphere at the time of the disturbance (tree-falls of unknown date, but probably in the early 1900s). Concentrations of these buried organic horizons were 24 μg/g compared to a modern organic horizon lead concentration of approximately 88 μg/g.

Regional Patterns in the Northeastern United States

During the 1960s and 1970s, soil samples were collected from a number of locations in the Northeast (Andresen et al., 1980; Johnson et al., 1982; Friedland et al., 1984b; Friedland et al., 1986a). All of these samples were analyzed for their trace-metal content (usually lead, copper, zinc, nickel, and cadmium). In 1978, the researchers collected forest floor samples from 40 sites in the mid-Atlantic states and southern New England. The survey was extended to include the rest of New England (excluding Maine) and more of the mid-Atlantic region for a total of more than 400 samples from 80 sites. Since 1980, forest-floor samples have been collected at random intervals. These samples have been archived for future reference to samples that will be collected during 1990 and

1991. These data will enable the descriptions of spatial patterns of trace metal concentrations and amounts in forest floors in the northeastern United States.

Known Effects of Trace Metals on Forested Ecosystems

Bioavailability and Biological Effects of Trace Metals

There are important differences between the concentration and amount of an element in the soil. Individuals concerned with the effects on biological organisms including plants will be more interested in the concentration of an element than the amount.

Rickard and Nriagu (1978) describe the chemistry of lead in soils as controlled by three parameters: (1) adsorption at the soil, mineral interface, (2) the formation of relatively stable organo-lead complexes and insoluble organo-lead particulates and chelates, and (3) the precipitation of relatively insoluble lead compounds. The relative importance of these three controlling factors varies depending on the type of ecosystem and ultimately determines the bioavailability of each element (Cataldo et al., 1987).

There are many methods for determining the speciation and mobility or bioavailability of trace metals in terrestrial ecosystems. Sequential extractions usually are conducted to determine the relative difficulty in removing successive fractions of trace metals from a soil or sediment (Miller et al., 1983). Because the results from sequential extractions are site- and procedure-dependent, it is difficult to generalize as to the relative fractions of metals in terrestrial ecosystems. In forests with abundant quantities of organic matter present, many authors have theorized that most of the trace metals are organically bound and there is relatively little "free" lead (Johnson et al., 1982).

A study of the relative fractions of trace metals in forest soil was conducted on a sandy soil underlying an oak forest in an industrial area of northwestern Indiana (Miller and McFee, 1983). In this study, the "O" (organic) horizon was removed and the upper 2.5 cm of mineral soil was used for the analysis of cadmium, zinc, copper, and lead fractions. The authors found that the largest fraction of most trace metals was bound to organic-matter, but there were substantial amounts held on soil exchange sites, and associated with carbonates and iron oxides. Lead had the highest percentage associated with organic matter (41.2%); cadmium the lowest (21%). It is important to realize that the percent organic matter (as estimated by loss on ignition) for the samples in this study ranged from 7.9 to 15.9, and the average was 9.7. In a forest floor, with loss-on-ignition of 50 to 70%, it is likely that the fraction of trace metals in the organically bound component would be substantially greater. Generally, lead complexation is related to organic matter content and carbonate levels in soil.

Regardless of the form and availability of the trace metals, they will have some effect on soil microorganisms. Many researchers have found that enzyme activity, CO_2 production, nitrogen mineralization, and numbers of microorganisms are lower in areas close to smelters or other point sources of pollution when compared with areas distant from pollution sources. It is known that extreme trace-metal concentrations (10^3 mg/kg or greater for lead, zinc, and nickel; 10^2 mg/kg or greater for copper, and 10 mg/kg or greater for cadmium) affect microbial respiration and soil organism populations (Ruhling and Tyler, 1970; Jackson and Watson, 1977). Several attempts have been made to determine the effects of moderate concentrations of trace metals on decomposition (Inman and Parker, 1978; Spalding, 1979; Friedland et al., 1986a). Low-to-moderate, trace-metal concentrations are of interest because the metal concentrations found in forests of the northeastern United States could be considered greater than "background levels" but much lower than concentrations found near smelters (Johnson et al., 1982; Friedland et al., 1986b).

Effects of Metals on Forest Floor Processes at Camels Hump, VT

Friedland et al. (1986b) reviewed a number of studies that assessed forest floor, litter, and organic soils and examined the effects of trace metals on soil microfauna, nitrogen mineralization, carbon dioxide evolution, and enzyme activities (Figure 1). Trace-metal concentrations (in single- or multiple-metal experiments) that were associated with a significant effect on one of the above parameters are shown with solid lines (Figure 1a). Those levels associated with no detectable effect are shown with broken lines (Figure 1b).

The maximum trace metal concentrations found at three sites in the northeastern United States are identified in Figure 1. For all five metals shown, (lead, copper, zinc, nickel, and cadmium), the concentrations found at Square Lake, ME, are well below concentrations necessary to significantly and noticeably alter soil biological activities. The concentrations of trace metals at Camels Hump, a mountain in the Green Mountains of Vermont, where research has been conducted for 10 years, are also below the concentrations that probably affect soil activities. Only the concentrations encountered near a zinc smelter in Palmerton, PA, are high enough to justify the conclusion that trace metal concentrations affect the activity of soil microorganisms.

However, it is quite possible that long-term exposure to the concentrations found at Square Lake, ME, or Camels Hump, VT, could alter species composition, species diversity, or other subtle measures of health, vigor, or resilience of a soil microorganism population. Current techniques of assessing chronic effects of trace metals in natural settings (i.e., in the forest) are probably not sensitive enough to detect any immediate adverse effects of metal concentrations such as those found on Camels Hump.

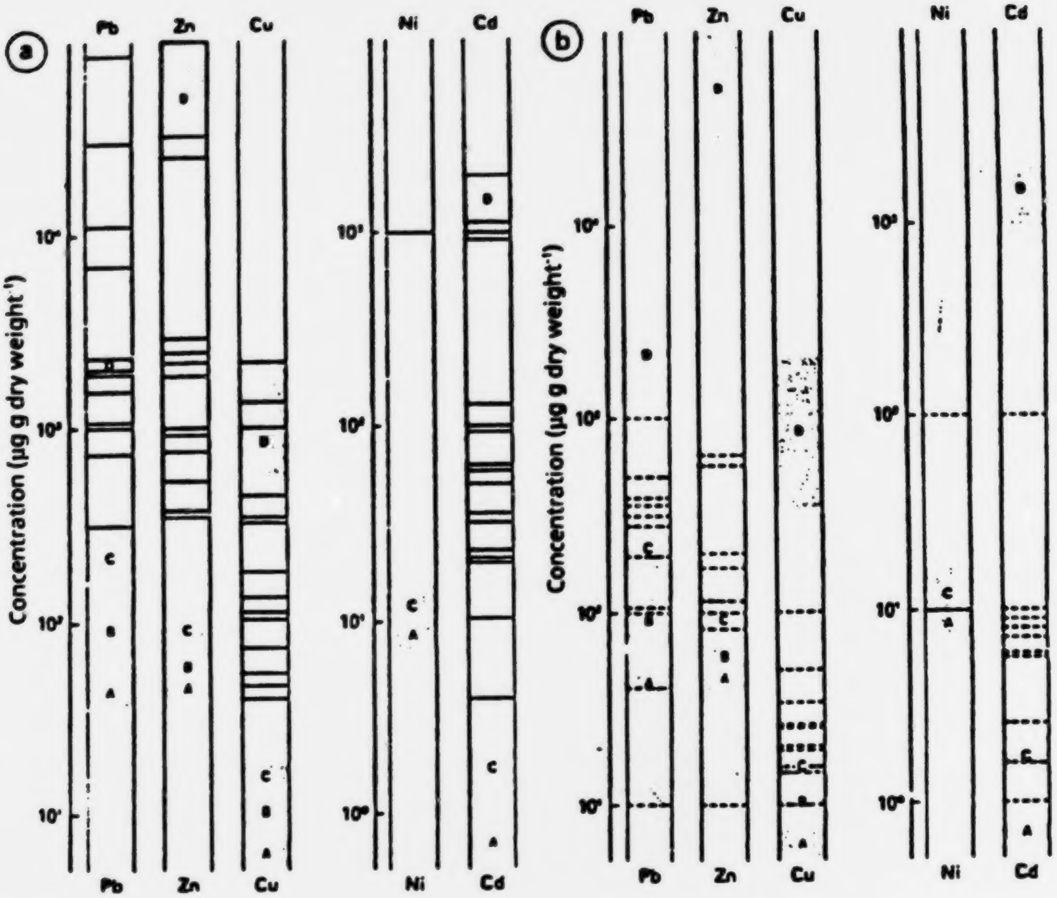

FIGURE 1. **Trace metal concentrations in organic matter at which CO_2 production, enzyme activity, litter accumulation, mineralization rate, or microbial populations were observed.** —, an effect of the metal was observed (a); —, no effect was observed (b). Metal concentrations are either found at the sampling site or those added by the investigator. Data in this figure were compiled from the studies reference in this paper. Metal concentrations for three localities in New England are also Shown: A, Square Lake, ME, (Fernandez and Czapkowsky, 1985); B, Camels Hump, VT, in 1966 (Friedland, Johnson and Siccama, 1984a); C, Camels Hump, VT, in 1980 (Friedland, Johnson and Siccama, 1984b); D, Palmerton, PA, (Buchauer, 1973). **Source**: Friedland et al., 1986b.

CONCLUSIONS

Trace metals have accumulated in the organic soils of forests in the northeastern United States. The concentrations of trace metals present in the forest floor at high-elevation sites such as Camels Hump, VT, are probably not high enough to interfere with soil organism activities, including organic matter decomposition. It is possible that trace metals have affected organic soil processes such as soil organism species composition and diversity.

ATMOSPHERIC DEPOSITION OF TRACE METALS TO LICHENS AND EFFECTS OF TRACE METALS ON LICHENS

Thomas H. Nash III

Department of Botany
Arizona State University
Tempe, AZ

INTRODUCTION

Lichens are symbiotic organisms composed of a photobiont (alga and/or cyanobacterium) and mycobiont (mostly *Ascomycotina*) that commonly occur as epiphytes, or as free-living organisms on rocks and soil. On a world-wide basis they are the dominant plant group on approximately 8% of the land surface (Larson, 1987) and are particularly prominent in polar regions. For example, Kershaw (personal communication) estimates that lichens dominate almost 40% of Canada. In addition, they are important components of many western and northern forests as epiphytes with biomasses as high as 700 to 3300 kg/ha (Boucher and Nash, 1990). In such forests finely dissected lichens may constitute over 50% of the canopy surface area, and hence are important in the interception of atmospheric aerosols.

One must recognize that lichens are fundamentally different from vascular plants and as a consequence may be better suited for metal deposition studies (Puckett, 1988). First, lichens possess no roots and have no other known mechanism for absorbing nutrients from soils. Therefore, they are largely dependent on atmospheric deposition for their nutrition (see below). Second, lichens possess no stomates or cuticular waxes and thus may take up atmospheric deposition over their entire surface areas. Third, lichens possess considerable intercellular space [(up to 20% of the volume in a *Xanthoria* species (Collins and Farrar, 1978)], that provides a repository for particulates. Furthermore, lichens are slow-growing perennials, many species of which may live hundreds of years. Because lichens do not shed parts (such as leaves for many vascular plants), their morphology remains uniform across seasons and years. As a consequence they provide uniform long-term receptors for atmospheric deposition. The fact that many lichens occur over wide geographical areas allows for both local and regional deposition monitoring. Finally, as discussed below, lichens have several mechanisms for taking up metals, and hence accumulate metals as the length of exposure to atmospheric deposition increases.

STATEMENT OF THE PROBLEM

Because of many of the ecological and morphological properties discussed above, lichens certainly are capable of intercepting atmospheric deposition of toxics. In addition, lichens are capable of retaining contaminants once intercepted and are therefore capable of providing useful biological monitors of trace metal deposition. On the basis of many studies of pollution source sites, elevated patterns near the pollution sources are well documented and therefore the trace metals must be retained. In addition, mechanisms for uptake and retention are well documented and principally include: (1) ion exchange, (2) intracellular uptake, and (3) particulate entrapment (Brown and Beckett, 1983; Nieboer and Richardson, 1981; Nash, 1989). Cell walls of the dominant sites, estimated variously as having a cation exchange capacity ranging from 6 to 77 μmol/g (Nash, 1989). These sites may become saturated in a matter of minutes when exposed to solutions of metals. By contrast, intracellular absorption occurs gradually over hours and follows Michaelis-Menten kinetic patterns. The magnitude of such internal absorption is generally much lower than external uptake at cell wall exchange sites. Even more important is particulate entrapment in intercellular spaces. This has been directly demonstrated by using scanning electron microscope (SEM) procedures in concert with an electron probe of the X-ray diffraction analysis of the particulates found with the SEM (Garty et al., 1979). The chemical profile of these particulates closely matches the known profile of particulates emitted from nearby pollution sources.

DEPOSITION OF TRACE METALS

Studies on metaliferous concentrations in lichens surrounding pollution source sites are numerous and well reviewed by James (1973), Nieboer and Richardson (1981), Puckett (1988), Puckett and Burton (1981). In most cases distinctly elevated concentrations are found near pollution sources as compared to areas farther away. In the absence of multiple pollution sources, concentrations may decrease logarithmically with distance (Nieboer and Richardson, 1981). Nieboer et al. (1978) summarized much of the early literature and initially constructed a table comparing elevated concentrations with background concentrations for a number of elements including metals. This information is edited to delete nonmetals and is further expanded to include metals not in the original tables (Table 1). The original table summarized baseline information from several locations. To illustrate the range of background data for individual regions, the recent investigations of Gough et al. (1988a) for epiphytes (*Hypogymnia* and *Usnea* species) from the northern coast area of California, and of Gough, et al. (1988b) for *Parmelia sulcata*, an epiphyte common in western North Dakota, and a variety of soil species from the Arctic (Puckett and Finegan, 1980) are also included.

This table needs to be interpreted with caution. Data for a few metals are poorly defined at the low end because of limits in detectability (less than symbols). Also, reported background concentrations may vary regionally with different substrates as is illustrated by the two data sets from Gough, et al. (1988 a,b) (Table 1). In addition, the widespread occurrence of industrialization within temperate latitudes may lead to relatively higher "background" levels than in areas of the world remote from industrialization. Interpretation of the elevated levels as concentrations toxic to, or tolerated by, the species is also problematic for several reasons. First, the viability of the specimens analyzed was rarely checked. Second, most of these values are for total metal contents and thus do not distinguish between metals found intracellularly and those found extracellularly (as particulates or at cell wall exchange sites). Finally, there are few polluted sites where only one metal is present. Most situations involve an array of metals and gaseous pollution and this potential toxicity needs to be assessed within a multivariate context and with a regard for potential interactions.

KNOWN EFFECTS OF TRACE METALS TO LICHENS

There are relatively few examples where a trace metal was demonstrably toxic to lichens in the field. One of the clearest examples, however, is for zinc toxicity, as documented by Nash (1972, 1975, 1989) surrounding a zinc smelter in Palmerton, PA. Zinc, cadmium, and sulfur dioxide were present near the smelter in sufficient concentrations to be toxic to some species. Because saturation soil extracts of zinc ions in concentrations toxic to at least some lichen species extended beyond the zone of detectability for sulfur dioxide, it was inferred that zinc was the principal toxic agent. At a control site 84 lichen species were found, but in the zone of extreme impact only nine species survived (Nash, 1972). Only two of the survivors, *Micarea trisepta* on rocks, and *Scoliciosporum chlorococcum* on trees, were abundant in the polluted site and both of these were of greater abundance in the polluted area than in the control area.

TABLE 1. COMPARISON OF BACKGROUND AND ELEVATED CONCENTRATION[illegible] (µg/g) OF CLASS A, BORDERLINE AND CLASS B METALS (NIEBOER AND RICHARDSON 1980).

Element	Background	References	Elevated	References
Class A Metals[a]				
Al	300-400 100-1800 1300-3000	Nieboer et al., 1978 Gough et al., 1988a Gough et al., 1988b	1300-1900 740-3700 900-4500	Nieboer et al., 1978 Olmez et al., 1985 Mueller et al., 1986
Ba	10-110 60-100	Gough et al., 1988a Gough et al., 1988b	367-487	Nash and Sommerfeld, 1981
Be	2-400	Nieboer et al., 1978		
Ca	$2\text{-}400 \times 10^{2}$ $12\text{-}130 \times 10^{2}$ $27\text{-}75 \times 10^{2}$	Nieboer et al., 1978 Gough et al., 1988a Gough et al., 1988b	$400\text{-}550 \times 10^{2}$	Nieboer et al., 1978
Ce	0.18-0.89	Gough et al., 1988a	2.2-7.2	Olmez et al., 1985
Cs	0-700	Nieboer et al., 1978		
Eu			0.03-0.13	Olmez et al., 1985
K	500-5000 620-2700 1375-1660	Nieboer et al., 1978 Gough et al., 1988a Puckett and Finegan, 1980	5000-9500	Nieboer et al., 1978
La	0.09-0.68	Gough et al., 1988a	1.7-5.6	Olmez et al., 1985
Li	0.09-0.55	Gough et al., 1988a	7.3-11.4	Nash and Sommerfeld, 1981
Lu			0.01-0.04	Olmez et al., 1985
Mg	100-1000 340-2600 540-1000 350-916	Nieboer et al., 1978 Gough et al., 1988a Gough et al., 1988b Puckett and Finegan, 1980	1000-12,000	Nieboer et al., 1978
Na	50-1000 120-560 159-233	Nieboer et al., 1978 Gough et al., 1988a Puckett and Finegan, 1980	1000-6000	Nieboer et al., 1978
Nd	0.09-.050	Gough et al., 1988a		
Sc	0.06-0.46 0.03-0.68	Gough et al., 1988a Puckett and Finegan, 1980	0.26-1.22	Olmez et al., 1985
Sm			0.17-0.70	Olmez et al., 1985
Sr	0-700 5.5-40 18-42	Nieboer et al., 1978 Gough et al., 1988a Gough et al., 1988b		

Table 1. (contd).

Element	Background	References	Elevated	References
Class A Metals (contd.)				
Tb			3.1-21	Olmez et al., 1985
Th			0.17-0.72	Olmez et al., 1985
U	0.5-1.0	Beckett et al., 1982	8.0-20.0 3.0-151.0	Beckett et al., 1982 Boileau et al., 1982
Y	0.06-0.37 1.3-3.8	Gough et al., 1988a Gough et al., 1988b		
Yb			0.06-0.25	Olmez et al., 1985
Borderline Metals				
As	0.60-1.5 0.26-0.44	Gough et al., 1988b Puckett and Finegan, 1980	2.6-8.0	Olmez et al., 1985
Cd	1-30 0.05-0.3	Nieboer et al., 1978 Gough et al., 1988a	30-330	Nieboer et al., 1978
Co	0.12-0.72 0.51-0.68	Gough et al., 1988a Puckett and Finegan, 1980		
Cr	0-10 0.34-13 5.6-11 1.5-2.3	Nieboer et al., 1978 Gough et al., 1988a Gough et al., 1988b Puckett and Finegan, 1980	25-130 up to 45	Nieboer et al., 1978 Vestergaard et al., 1986
Fe	50-1600 360-1900 1600-3900 50-3560	Nieboer et al., 1978 Gough et al., 1988a Gough et al., 1988b Puckett and Finegan, 1980	400-90,000 up to 17,000 4875-14,400	Nieboer et al., 1978 Vestergaard et al., 1986 Noeske et al., 1970
Ga	0.09-0.49	Gough et al., 1988a	0.2-2.2	Olmez et al., 1985
Mn	10-130 40-330 57-110 30-85	Nieboer et al., 1978 Gough et al., 1988a Gough et al., 1988b Puckett and Finegan, 1980	300-5000 326-466	Nieboer et al., 1978 Nash and Sommerfeld, 1981
Ni	0-5 3.4-26 4-17 2.5-2.9	Nieboer et al., 1978 Gough et al., 1988a Gough et al., 1988b Puckett and Finegan, 1980	10-300 up to 25	Nieboer et al., 1978 Vestergaard et al., 1986

Table 1. (contd).

Element	Background	References	Elevated	References
Borderline Metals				
Sb	0.08-0.13	Puckett and Finegan, 1980		
Sn	0.9-4.4	Gough et al., 1988a		
Ti	6-150	Nieboer et al., 1978	150-3800	Nieboer et al., 1978
	5.6-88	Gough et al., 1988a	100-240	Nieboer et al., 1982
	12-19	Gough et al., 1988b		
	48-68	Puckett and Finegan, 1980		
V	0-10	Nieboer et al., 1978	10-300	Nieboer et al., 1978
	0.21-6.3	Gough et al., 1988a	10-20	Schwartzman et al., 1987
	2.7-5.7	Gough et al., 1988b	10-58	Nygard and Harju, 1983
	1.0-2.0	Nygard and Harju, 1983		
	1.2-4.0	Puckett and Finegan, 1980		
Zn	20-500	Nieboer et al., 1978	1000-25000	Nieboer et al., 1978
	9.1-40	Gough et al., 1988a	up to 2100	Vestergaard et al., 1986
	60-320	Gough et al., 1988b		
	16-25	Puckett and Finegan, 1980		
Class B Metals				
Cu	1-50	Nieboer et al., 1978	15-1100	Nieboer et al., 1978
	1.3-10	Gough et al., 1988a	1000-4900	Alstrup and Hansen, 1977
	12-120	Gough et al., 1988b	up to 160	Vestergaard et al., 1986
	6.2-8.5	Puckett and Finegan, 1980		
Hg	0-1	Nieboer et al., 1978	7.9-29	Lodenius, 1981
	0.12-0.16	Gough et al., 1988b	2-8	Bargagli et al., 1987
Pb	5-100	Nieboer et al., 1978	100-12,000	Nieboer et al., 1978
	3.6-20	Gough et al., 1988a	up to 950	Tomassini et al., 1976
	4.2-5.6	Puckett and Finegan, 1980	up to 600	Schwartzman et al., 1987
			up to 3000	Jones et al., 1982
			1740-2750	Noeske et al., 1970

[*] These three classes of metals fall into natural groups within the periodic table of chemical elements and may be divided by a covalent index that reflects different ligand binding affinities. Class A metals prefer O-N-S donors, whereas Class B prefer S-N-O donors and borderline metals fall in between.

In the Sudbury nickel mining complex in Ontario, Canada, *Scoliciosporum chlorococcum* was the only epiphytic lichen found on *Populus balsamifera*, a widely planted tree in the zone where the original forest was destroyed (LeBlanc et al., 1972). Both the *Stereocaulon* and *Cladonia* species on soils and *Umbilicaria* species on rocks can still be found at distances from the smelters. Tomassiniet al. (1976) measured Ni concentrations up to 220 to 310, Fe up to 17800 to 5200, and Cu up to 250 µg/g. Similarly, in the vicinity of a steel complex in England, Seaward (1973) reports concentrations (µg/g) in *Peltigera rufescens* as high as 90,000 Fe, 5000 Mn, 91 Cu, 127 Cr, 454 Pb, and 38 Ni. A *Cladonia* and *Coleocaulon* species had somewhat lower concentrations. In the city of Leeds values up to 35,800 Fe, 349 Mn, 159 Cu, 97 Cr, 3124 Pb, and 183 Ni are reported for *Lecanora muralis*. Other studies are incorporated into Table 1 and could easily be discussed further here. For example, the numerous investigations of the areas surrounding electrical power plants could be summarized, but the release of metals from power plants is frequently an order of magnitude lower than that which occurs near smelters.

POTENTIAL EFFECTS

Metals may well become toxic if accumulated within the cytoplasm. Cytological effects are not well documented in lichens, but generally it is known that binding centers in proteins and enzymes satisfy the reactivity requirements of class A, class B, or borderline ions. Specificity of metals occupying these binding centers is related to their size and geometry as well as ligand type. Ochiai (1977) therefore divided mechanisms of metal-ion toxicity into three categories: (1) blocking of the essential biological function groups of proteins and enzymes, (2) displacing the essential metal ion in proteins and enzymes, or (3) modifying the active conformation of proteins and enzymes. There is good evidence that at least some lichens are tolerant of higher internal concentrations of metal ions than other lichens (see discussion above), but particular cellular mechanisms that allow such tolerance are not currently known. Thus, it may be useful in future studies to determine if the tolerant species (ecotypes, etc.) possess some specific cellular mechanism for preventing toxicity by one or more of the mechanisms discussed by Ochiai (1977).

RESEARCH RECOMMENDATIONS

There is a definite need to determine the degree to which toxics, including both trace metals and synthetic organics, are distributed within the U.S. as well as around the globe. Therefore, it is timely that major monitoring programs such as the U.S. EPA's Environmental Monitoring and Assessment Program (EMAP) be initiated. Because there is evidence for long distance transport of toxics to the Arctic where cooler atmospheric temperatures act as a huge distillation column for the organics in particular, it may well be appropriate for an initial concentration of studies to be planned there. In polar regions, lichens should be the organism of choice to provide biological monitoring to supplement instrumented monitoring stations to achieve greater local and regional detail on deposition patterns. A joint Canada-U.S. program, perhaps developed cooperatively between Environment Canada and the U.S. EPA. Ideally, the program should be expanded to include the Soviet Union, and this may be possible through the joint U.S.-U.S.S.R. program on Air Pollution Effects on Vegetation.

Concurrent with the field studies, there should also be laboratory studies with lichens. There should be studies for toxics that have not previously been well investigated, to: (1) determine lichen uptake kinetics and retention characteristics, and (2) define dose-response relationships for toxics. In the latter case, there is very little information, particularly for synthetic organics.

CONCLUSIONS

An important question raised concerning the need for an air toxics program is: "where are the dead bodies?" The short answer is, decomposed and disappeared. In the case of lichens, we know that major declines in the lichen flora of urban and industrial areas have occurred on all continents (Nash and Wirth, 1988). In addition, regional level declines are known. Gaseous pollutants, such as sulfur dioxide and hydrogen fluoride, are known to occur in sufficient concentration to be detrimental to many lichen. Some of the less studied airborne contaminants may also occur in sufficiently high concentrations to be toxic. One need only reflect that as recently as the early 1950s, ozone, the air pollutant currently recognized as a regionally important phytotoxic agent, was not even identified as an air pollutant. To determine which of the air toxics are really ecologically important will require both a monitoring program and effects research.

FATE AND EFFECTS OF PAHs IN THE TERRESTRIAL ENVIRONMENT:
AN OVERVIEW

Nelson T. Edwards

Environmental Sciences Division
Oak Ridge National Laboratory
Oak Ridge, TN

INTRODUCTION

A recent review of polycyclic aromatic hydrocarbons (PAHs) in the terrestrial environment (Edwards, 1983) pointed to the need for more information and a better understanding of factors controlling the fate of PAHs. With ever-increasing energy demands by a growing world population, the amount of PAHs released from energy-producing technologies becomes potentially greater. When PAHs are released into the atmosphere in the vapor phase, most are adsorbed to particles (e.g., fly ash). They are also found in solid and liquid wastes from various energy technologies. Polycyclic aromatic hydrocarbons released to the atmosphere may be carried hundreds of kilometers from the source before being deposited on vegetation and soil. The well-known PAHs such as benzo[a]pyrene (B[a]P) are innocuous by themselves, but can be biologically activated by enzymes to form epoxides that are carcinogenic and mutagenic (Levin et al., 1978). This report summarizes our knowledge about PAHs in the terrestrial environment with emphasis on their fate and effects on vegetation.

SOURCES OF PAHs

Polycyclic aromatic hydrocarbons are found throughout the world in water, air, soil, and the biota. The ubiquitous nature of PAHs may be a consequence of synthesis in terrestrial vegetation (Andelman and Suess, 1970). Suess (1976) and Shabad (1980) pointed to microbial synthesis, higher plant synthesis, and volcanic activity as major contributors to the natural background levels of PAHs, but emphasized that quantities of PAHs formed by natural processes are very small in comparison to those from anthropogenic sources. Blumer (1961) suggested that PAHs found in rural soil remote from major highways and industries cannot be attributed totally to air pollution, but are instead endogenous to soil. However, Lunde and Bjorseth (1977) demonstrated that PAHs are transported over relatively long distances from industrial areas of England, France, and Scotland. Conversely, Lyall et al. (1988) presented evidence of very little transport of PAHs from urban to rural areas in Australia. Graf and Diehl (1966) grew plants in a PAH-free nutrient solution and concluded from the results that plants can synthesize PAHs. However, Grimmer and Düvel (1970) found that plants grown in filtered air contained no detectable PAHs, whereas their counterparts in unfiltered air did contain PAHs.

The major anthropogenic sources of PAHs are those resulting from conversion of fossil fuels, refuse burning, and agricultural burning. The origin of most PAHs is through high-temperature pyrolysis of various naturally occurring organic materials (e.g., coal). Seuss (1976) estimated global B[a]P emissions during 1968 to be about 4570 metric tons, mostly from fossil fuel burning (Table 1). Estimated annual B[a]P emissions in the United States in 1968 ranged from 1000 metric tons (Guerin, 1978) to 1700 metric tons (NAS, 1972). Guerin (1978) estimated 640 to 780 metric tons of B[a]P emissions in the United States in 1972 (Table 1). Nearly half of this total came from heating and power, mostly from residential furnaces and fireplaces.

Coal-fired steam plants contributed less than 1 metric ton/y. Gasoline- and diesel-powered vehicles contributed >2% of the total B[a]P emissions. However, this number can be misleading because other PAHs (e.g. coronene) are found in higher concentrations in vehicular exhaust than B[a]P. Lyall et al. (1988) sampled eight PAHs in the Latrobe Valley in Australia and found that the motor vehicle was the main contributor to PAH contamination of the atmosphere and that domestic heating added a significant contribution during cold weather. They found that coal-fired power plants added very little to the atmospheric PAH concentrations. However, if used on a large scale, coal conversion processes could have a significant effect on anthropogenic input of PAHs to the environment. Reports of high releases of potentially hazardous chemicals from coal gasification plants support this hypothesis. Analysis of gas, liquid, tar, and solid effluents from coal-fueled gasifiers showed PAHs to be of special concern (Cleland, 1981). For example, B[a]P ranked near the top of the list as a potentially hazardous chemical in the gas and tar streams, with a relatively high discharge rate in the liquid stream. Maximum discharge concentration of B[a]P in the gaseous stream of one of the gasifiers was 5000 mg m^{-3}, and the concentration in tar was 3500 mg/g. Total B[a]P discharged was 120 mg/g of coal.

TABLE 1. ESTIMATED ANNUAL EMISSIONS OF BENZO[a]PYRENE (B[a]P) IN THE UNITED STATES AND GLOBALLY.

	B[a]P Emissions (metric tons/y)	
Sources	U.S.[a]	Global[b]
Heating and Power		
Coal fired residential furnaces	270	-[c]
Coal intermediate sized furnaces	6	-
Wood, home fireplaces	23	-
Coal, steam power plants	<1	-
Oil, residential heating	2	-
Gas, residential heating	2	-
Total	304	2360
Industrial Processes		
Coke production	0.05-153	
Petroleum catalytic cracking	6	-
Total	6-153	950
Enclosed Incineration	3	90
Coal Refuse Burning	281	620
Forest and Agricultural Fires	10	380
Other Burning		
Vehicle disposal	5	-
Other open burning	9	-
Total	14	130
Vehicles		
Diesel powered	<1	-
Gasoline powered	10	-
Rubber tire degradation	10	-
Trucks and buses	-	30
Automobiles	-	10
Total	21	40
Grand Total	640-780	4570

[a] From Guerin (1978)
[b] From Suess (1976)
[c] No data available.

Not enough data have been collected to estimate total PAH emissions (other than B[a]P) from anthropogenic sources. It is generally accepted, however, that B[a]P represents only a small percentage of the total and that anthropogenic sources are far greater than natural sources.

PAH CONCENTRATIONS IN AIR, SOIL, AND VEGETATION

Concentrations of PAHs in air vary greatly, both spatially and temporally. Sawicki et al. (1960) examined the B[a]P content of air in 131 urban and nonurban areas of the United States. In nine large cities the highest levels of B[a]P occurred during winter months, and the lowest levels occurred during summer. Concentrations of B[a]P in the air of nonurban areas ranged from 0.01 to 1.9 ng/m^3, whereas concentrations in urban areas ranged from 0.1 to 61.0 ng/m^3. Gordon (1976) reported the annual geometric mean concentration of 15 PAHs in air samples collected from 13 areas in Los Angeles County, CA, to be 10.9 ng/m^3. Concentrations of B[a]P only accounted for 4.2% of the total.

Relatively few studies have quantified PAH concentrations in soil and vegetation at various distances from known sources. Typical concentrations of B[a]P in soils of the world ranged from 2100 to 1000 ng/g. A typical range for total PAHs is about 10 times the value for B[a]P alone. The actual measured range of B[a]P concentrations in soil, including data from very highly polluted areas and from protected remote regions, is 0.4 ng/g (Shabad et al., 1971)) to 650,000 ng/g (Fritz, 1971).

Although PAH concentrations in the environment have increased, our knowledge of their movement through terrestrial food chains has remained static. Results from past research on the uptake, conversion, and concentration of PAHs by vegetation are conflicting. A book by Grimmer (1983) on PAHs devoted only 4 of 250 pages to contamination of food, with no references to PAH movement through terrestrial food chains.

Not enough data are available on a sufficient number of different PAHs (most research has been with B[a]P only) to make reasonable predictions about their food chain transfer and accumulation rates. Results from previous research do suggest, however, that PAHs can enter the food chain by contamination of vegetation. Concentrations of 16 PAHs in garden vegetables collected 3 km downwind from a coal-fired power plant in Tennessee ranged from 8 ng of total PAHs/g dry weight of lettuce roots to 107 ng/g of lettuce leaves (Table 2). The PAHs found in greatest concentrations were fluoranthene, phenanthrene, and acenaphthylene. B[a]P averaged only 2% of the total PAH contamination. Previously reported concentrations of B[a]P in vegetation ranged from 0.1 (Kolar et al., 1975) to 150 ng/g (Fritz, 1971), with typical concentrations of 1 to 10 ng/g. Much greater PAH concentrations were found in vegetation growing adjacent to a tar waste pit located <2 km from a coal gasification plant in Tennessee (Table 3). This site was expected to have potential for both high inputs of PAHs from the atmosphere and high uptake via plant roots from the tar waste pit. Total PAH concentrations in roots ranged from 534 ng/g in *Carex* sp. to 6401 ng/g in lambs quarters

TABLE 2. PAH CONCENTRATIONS IN GARDEN VEGETABLES COLLECTED FROM 8 KM SOUTHWEST OF A COAL-FIRED STEAM PLANT IN EASTERN TENNESSEE (SITE A) AND FROM 3 KM NORTHEAST OF THE SAME STEAM PLANT (SITE B)[a].

PAH	Site A			Site B		
	Radish Leaves	Spinach Leaves	Lettuce Leaves[b]	Lettuce Leaves	Lettuce Leaves[b]	Lettuce Roots[b]
Naphthylene	-[c]	-	-	-	-	4
Acenaphthylene	20	12	11	25	5	<1
Acenapthene	-	-	-	-	-	<1
Fluorene	-	2	1	4	<1	<1
Phenanthrene	36	9	4	6	<1	<1
Anthracene	13	-	-	<1	<1	<1
Fluoranthene	19	13	28	49	5	2
Pyrene	9	8	3	6	<1	<1
Benz[a]anthracene	2	1	<1	11	<1	<1
Chrysene	2	-	1	1	<1	-
Benzo[a]fluoranthene	4	2	1	2	<1	<1
Benzo[k]fluoranthene	2	1	<1	<1	<1	<1
Benzo[a]pyrene	1	1	<1	1	<1	<1
Dibenz[a,h]anthracene	2	2	<1	1	<1	-
Benzo[ghi]perylene	<1	1	-	-	-	-
Indeno(1,2,3-*cd*)pyrene						
TOTAL	110	52	53	107	41	8

[a] All values are in nanograms per gram.
[b] Samples were rinsed with cold water.
[c] Concentrations were not detectable.

(*Chenopodium album* L.), a perennial forb. Concentrations in leaves ranged from 14 ng/g in Johnson grass (*Sorghum halepense* L.) to 562 ng/g in *Carex* sp. The average concentrations were 2584 ng/g in roots and 294 ng/g in leaves. The B[a]P concentrations ranged from 0.2 to 13.5% of the total PAH concentration, varying with both plant species and plant organs in no consistent patterns. Polycyclic aromatic hydrocarbons found in greatest concentrations in roots were anthracene, acenaphthylene, phenanthrene, and fluoranthene. Those found in greatest concentrations in leaves were fluoranthene, acenaphthylene, indeno (1,2,3-*cd*) pyrene, chrysene, and anthracene. Fluoranthene and benzo[a]anthracene were found in relatively high concentrations (340 and 459 ng/g, respectively) in stems of a sycamore tree (*Platanus occidentalis* L.). Concentrations of PAHs in vegetation are generally less than those in the soil. Bioconcentration factors (concentration in vegetation/concentration in soil) reported in the literature range from 0.002 to 0.33 for B[a]P.

TABLE 3. PAH CONCENTRATIONS IN VEGETATION COLLECTED PROXIMALLY TO A COAL TAR BURIAL TRENCH AND < 3 KM FROM A COAL GASIFICATION PLANT IN EASTERN TENNESSEE.[a]

PAH	Carex[b] Roots	Carex[b] Leaves	J. Grass Roots	J. Grass Leaves	L. Quarters Roots	Ragweed Leaves	Sycamore Stems
Naphthylene	-[c]	-	-	-	-	-	12
Acenapthene	142	89	193	1	774	15	67
Fluorene	-	29	44	-	25	-	-
Phenanthrene	56	-	34	<1	733	41	10
Anthracene	-	61	-	<1	1972	-	1
Fluoranthene	118	45	-	-	675	98	340
Pyrene	84	31	94	-	530	46	39
Benz[a]anthracene	13	11	64	-	75	22	459
Chrysene	67	44	735	-	-	23	-
Benzo[a]fluoranthene	9	27	100	<1	216	20	1
Benzo[k]fluoranthene	8	5	50	<1	37	8	1
Benzo[a]pyrene	10	13	111	<1	92	17	2
Dibenz[a,h]anthracene	18	21	59	10	168	16	2
Benzo[ghi]perylene	31	28	24	<1	143	13	-
Indeno(1,2,3-*cd pyrene*)	40	81	-	<1	226	9	3
Total	534	562	817	14	6401	305	960

[a] All values are in nanograms per gram.
[b] Carex=*Carex* sp.; J. Grass=Johnson grass; L. quarters=Lambs quarters; Ragweed=*Ambrosia* sp.
[c] Concentrations were not detectable.

Only one paper reported PAH data (other than just B[a]P data) for both plants and soil from the same location. Wang and Meresz (1981) analyzed garden vegetables and soil for 17 PAHs, including B[a]P, and found most of the PAH contamination in the peels. Their vegetation/soil concentration ratios ranged from 0.0001 to 0.085 for B[a]P and 0.001 to 0.183 for total PAHs. The amounts and kinds of PAHs ingested by humans and other animals from vegetation are partially dependent on whether PAHs are absorbed versus adsorbed, and how easily they are rinsed off with water. Kveseth et al. (1981) suggested that lower molecular weight PAHs are adsorbed on leaves, whereas higher molecular weight particulated compounds are washed off by rain. Kolar et al. (1975) found that washing vegetables removed a maximum of 25% of PAH contamination and generally less. However, the data presented in Table 2 demonstrate that 87% of the total PAH mass over a wide range of molecular weights is removed from lettuce by rinsing the leaves in cold water.

PAH UPTAKE, TRANSLOCATION, AND METABOLISM IN VEGETATION

Relatively few experiments have been conducted that address questions relating to the uptake and translocation of PAHs in vegetation. Graf and Nowak (1966) demonstrated growth stimulation of tobacco, rye, and radishes by a number of PAHs, including B[a]P, and concluded that the compounds were assimilated through the roots. Gunther et al. (1967) found no translocation of several PAHs from orange rind (point of application) to other plant parts, and Harms (1975) reported negligible translocation of ^{14}C-B[a]P from wheat roots to shoots. Edwards et al. (1982) reported both the uptake of ^{14}C-anthracene from nutrient solution into *Glycine max* Merr. (soybean) roots and translocation to leaves, and the negligible uptake from air into leaves and translocation to roots. However, Ellwardt (1977) concluded, from field experiments with fresh compost containing a number of PAHs and with several agricultural crops, that little or no uptake by plant roots occurred.

The rate (amount/unit time) of PAH uptake by plants is dependent on a number of factors, including PAH concentration and plant species. Deubert et al. (1979) found that *Zea mays* L. (corn) and *Triticum aestivum* L. (wheat) seeds absorbed B[a]P in proportion to B[a]P concentrations in water used for soaking the seeds. Edwards et al. (1982) found that ^{14}C-anthracene uptake by soybeans from a nutrient solution was directly proportional to anthracene concentration in the solution. Several studies (Shabad et al., 1971; Shabad and Cohan, 1972; Linne and Martens, 1978) have demonstrated differences in assimilation rates with different plant species.

Other factors that affect PAH uptake rates by plants include the nature of the substrate in which the plant is growing, PAH solubility, PAH phase (vapor or particulate), and molecular weight. Dörr (1970) found no uptake of B[a]P by *Triticum* spp. (wheat) and *Secale cereale* L. (rye) from nutrient solution or soil when B[a]P was applied in insoluble form (i.e., not dissolved in oil or some other solvent). However, uptake and translocation did occur when B[a]P was dissolved in oil before applying to the substrate. Recent research (N.T. Edwards, unpublished data) demonstrated good correlation between PAH uptake rates by bean plants from nutrient solution and the relative aqueous solubilities of anthracene (ANTH), B[a]P, and benzo[a]anthracene (B[a]A). Müller (1976) reported greater uptake of ^{14}C-B[a]P by vegetable plants growing in sand culture when the ^{14}C-B[a]P was applied dissolved in benzene rather than when the ^{14}C-B[a]P was dissolved in plant oil or detergent. Müller also reported greater uptake of B[a]P by plants growing in sand than those growing in soil and compost. Dörr (1970) reported greater uptake of B[a]P by rye from nutrient solution than from soil, but reported no effect of different soil types on uptake rates. Edwards et al. (1982) found that 87% of the total ANTH dosage was assimilated by soybean plants from a nutrient solution over a four-day period, but only 7% was assimilated over the same time period from soil containing the same ANTH dosage. In a related five-day experiment, twice as much ANTH and/or its metabolites was assimilated by bush bean plants from soil containing ANTH in solution as from soil containing ANTH adsorbed to fly ash (N.T. Edwards, unpublished data). Nearly 90% of the ANTH assimilated from the fly ash soil was retained in the roots, whereas only 50% of that assimilated from soil solution was retained in the roots, with the remainder translocated to stems and leaves (Figure 1).

Although relatively little is known about PAH uptake and translocation in terrestrial plants, even less is known about the chemical fate of these compounds within plants. Dörr (1970) found a decline in B[a]P concentrations in rye plants after 30 days of growth, following a period (20 days) of increasing concentrations through uptake from nutrient solution and soil. The decline in B[a]P concentration was attributed to degradation or chemical changes of the B[a]P within the plants. *Phaseolus vulgaris* L. (bush bean) plants grown for 30 days in nutrient solution containing ^{14}C-labeled ANTH, B[a]A, or B[a]P assimilated, respectively, 64, 66, and 41% of the total ^{14}C dosage (N.T. Edwards, unpublished data). Only 6, 1, and 0.5% of the total ^{14}C dosage associated with ANTH, B[a]A, and B[a]P, respectively, was translocated to the stems and leaves. Of the ^{14}C extracted from the plants, these compounds were in the form of polar metabolite compounds of ANTH, B[a]A, or B[a]P: more than 95% of that from the leaves and 82 to 97% of that from the stems (Figure 2). Extremely small fractions of the extractable ^{14}C in the stems and leaves were associated with the parent PAH compounds. In the roots, however, 26, 27, and 65% of the ^{14}C was associated with B[a]P, ANTH, and B[a]A, respectively, indicating that B[a]A was the most resistant of the three PAHs to metabolism by the plant.

Thus, although conclusions vary widely between experiments, and much more research is needed, a consensus would suggest that PAHs can enter the food chain by contamination of vegetation. The seriousness of this problem depends in part on molecular species and contamination levels, and in part on degradation rates and degradation products in air, soil, and vegetation.

PAH DEGRADATION

Degradation usually implies a reduction in chemical complexity of a compound and is often thought of as a process that will change a hazardous compound to an innocuous one. However, some nonhazardous compounds may be altered chemically to form hazardous compounds. For example, B[a]P is innocuous but can be biologically activated by enzymes to form epoxides that are carcinogenic and mutagenic. In the discussion that follows, the term degradation means simply a chemical modification. Besides metabolism by green plants discussed above, the major ways that PAHs are degraded in the terrestrial environment are by photochemical oxidation and metabolism by microorganisms.

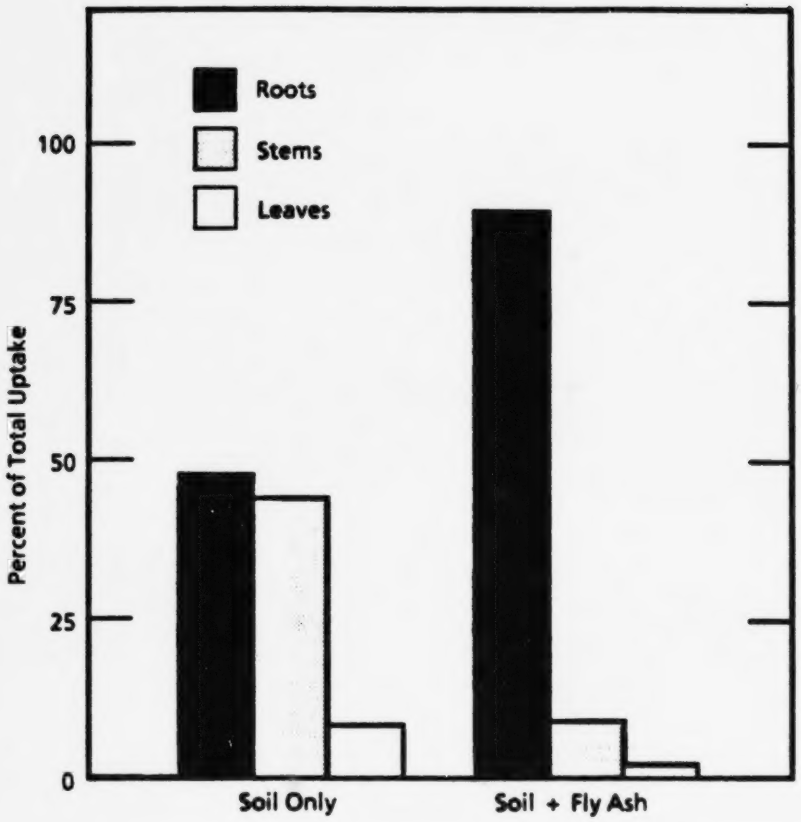

FIGURE 1. A comparison of the distribution of ^{14}C-ANTH or its metabolites in *Phaseolus vulgaris* L. after 5 days growth in soil containing fly ash that had been previously vapor phase coated with ^{14}C-ANTH, or in soil containing ^{14}C-ANTH in solution.

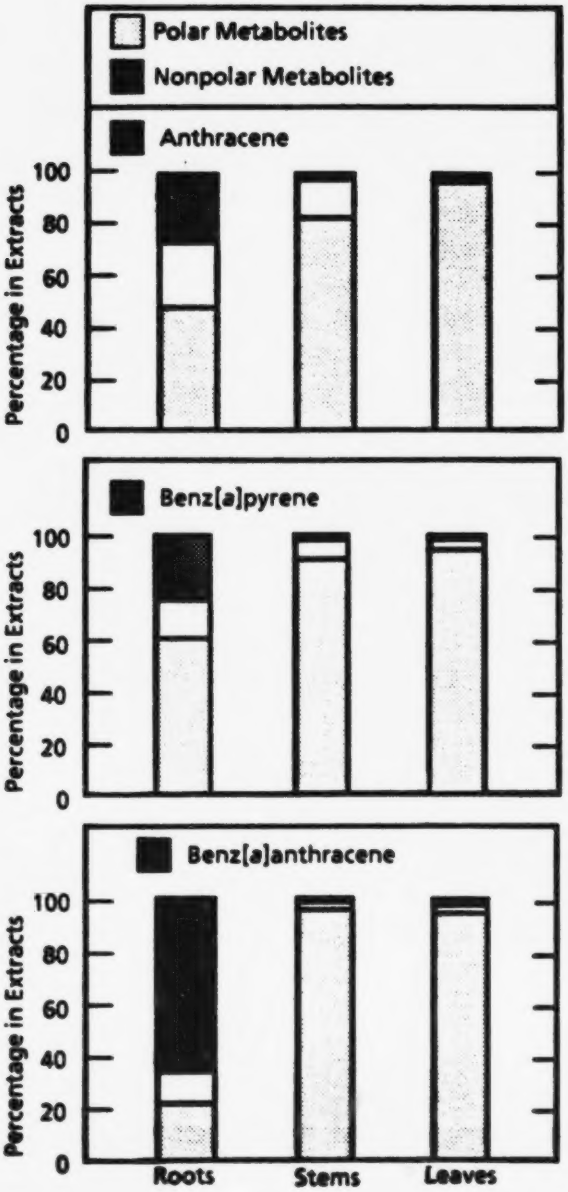

FIGURE 2. A comparison of the distribution of ^{14}carbon labeled PAHs and metabolites in *Phaseolus vulgaris* L. after 30 days growth in nutrient solution containing ANTH, B[a]A, or B[a]P.

Photooxidation may be one of the most important processes in the removal of PAHs from the atmosphere (NAS, 1972). Yet some of the reaction products may also be carcinogenic, making it risky to evaluate carcinogenicity solely on PAH content (Fox and Olive, 1979). One of the more common photooxidation reactions of PAHs is the formation of endoperoxides that ultimately undergo a series of reactions to form quinones (NAS, 1972). Katz et al. (1979) observed that B[a]P is photooxidized to B[a]P quinones that are direct-acting mutagens. They found the reactions to occur faster when B[a]P was irradiated in the presence of ozone. Evidence for faster PAH degradation in the presence of ozone is supported by Lyall et al. (1988) and by Blokzijl and Guicherit (1972) who reported greater photooxidation of PAHs in summer than in winter, presumably as a result of higher temperatures, but possibly because of the combined effects of higher temperatures and elevated tropospheric ozone concentrations in the summer months. Evidence exists that discredits the widely held belief that particulate association of PAHs will promote their photooxidation. For example, B[a]P, pyrene, and ANTH will photooxidize efficiently in liquid solution, but are highly resistant to photooxidation when adsorbed on fly ash (Korfmacher et al., 1980).

Degradation of PAHs by microorganisms has been demonstrated in a number of investigations. Groenewegen and Stolp (1981) isolated microorganisms that can use naphthalene, anthracene, and phenanthrene as their sole carbon source. However, they could show degradation of some of the PAHs that are less water-soluble (e.g., B[a]A and B[a]P) only when the PAHs were mixed with soil, water, and a substance to stimulate growth of oxygenase-active organisms. Shabad et al. (1971) discussed several experiments that demonstrated bacterial degradation of B[a]P in soil. They found that the capacity of bacteria to degrade B[a]P increased with B[a]P content in the soil and that the microflora of soil contaminated with B[a]P were more active in metabolizing B[a]P than those in "clean" soil. Biochemical pathways for the degradation of a number of PAHs by soil microorganisms have been proposed (Evans et al., 1965; Gibson et al., 1975).

EFFECTS OF PAHs ON PLANTS

The limited amount of research that has been performed on the effects of PAHs on plants indicates that PAHs may act as regulators of plant growth and morphogenesis. Graf and Nowak (1966) observed that B[a]P and other PAHs stimulated the growth of algae and higher plants in solution culture, and suggested that PAHs synthesized by plants may act as plant growth hormones.

Wettig et al. (1976) germinated several species of vegetable and grain seeds in hydroponic systems, with and without an added carbon source, and found that the seeds with the added carbon increased in B[a]P content. Borneff et al. (1968a; 1968b) demonstrated that algae can synthesize some PAHs from ^{14}C-acetate added to their growth medium. Reinert (1952) demonstrated stimulatory or inhibitory effects of B[a]P on the growth of fern prothallia depending on concentrations used. Forrest et al. (1989) observed earlier morphological transitions and accelerated cell proliferation in B[a]P-treated fern prothallia than in untreated controls. However, B[a]P concentrations greater than 0.32 μg/mL inhibited cell proliferation in the fern prothallia, and concentrations of 10 μg/mL or higher decreased spore germination and plant survival. Benzo[a]anthracene stimulated tobacco callus tissue cell differentiation into roots and shoots (Kochhar et al., 1970). Similarly, 7-12-dimethylbenzo[a]anthracene stimulated callus tissue of *Hawortha variegata* to differentiate into roots and shoots (Majumdar and Newton, 1972).

CONCLUSIONS

A number of conclusions about the fate of PAHs in the terrestrial environment can be drawn from past research. These conclusions can be generally stated as follows: (1) vegetation can assimilate PAHs from soil through the root systems, but plant/soil bioaccumulation factors are generally <1; (2) assimilation rates vary with substrate, plant species, phase (whether adsorbed to particles or in solution), concentration, and chemical properties (e.g., solubility in water) of the individual PAHs; (3) PAHs are scavenged from the air by plant leaves and remain primarily on the surface, but are available for wash off to the soil; and (4) PAHs are chemically transformed by soil microorganisms, by vegetation, and by photooxidation especially at warm temperatures and high ozone concentrations. Reported results on the fate of PAHs are incomplete (most studies have concentrated on B[a]P only), and there is a need for research in this area. Studies should include not only PAHs that have been identified as having carcinogenic potential (such as B[a]P) but also all PAHs frequently found in the environment. Perhaps the most pressing questions concerning the fate of PAHs in the terrestrial environment are these: (1) what are the products of PAH metabolism in air, soil, and vegetation, and (2) what is the fate of those metabolic products? Studies of effects indicate that PAHs may act as regulators of plant growth and morphogenesis. However, given the paucity of studies dealing with the effects of PAHs on vegetation (most studies have been conducted on simple algae or at the cellular and tissue culture level in higher plants), new initiatives in this area of research are needed and should be given high priority. Such studies should examine the effects of PAHs on the growth and physiology of genetically similar higher plants established at sites known to be contaminated and at selected control sites in order to extrapolate results to the community and ecosystem level. Mechanistic studies could be conducted under more controlled conditions.

EFFECTS OF ORGANIC CHEMICALS IN THE ATMOSPHERE ON TERRESTRIAL PLANTS

Jeffrey R. Foster

Holcomb Research Institute
Butler University
Indianapolis, IN

INTRODUCTION

Thousands of organic compounds are released into the atmosphere each year by human activity. Of these, the U.S. Environmental Protection Agency (EPA) has classified 328 as Priority Pollutants, based on scientific evidence of toxicity in humans and other animals. However, only two, benzene and vinyl chloride, have National Ambient Air Quality Standards. Until recently, our knowledge of environmental releases of these substances was sketchy. In 1986, Congress passed the Emergency Planning and Community Right-to-Know Act, requiring manufacturers of Priority Pollutants to report the amounts of each that they released, deliberately or accidentally, into air, water, and soil. The results of the first round of the Toxic Release Inventory (TRI) revealed that 865,000 metric tons of toxic organic compounds were released to the atmosphere in 1987 (US EPA, 1989). Small manufacturers (<3,400 kg/year) and end users (e.g., farmers applying pesticides) were not required to report, and no attempt was made to incorporate emissions from area sources (dry cleaners, motor vehicle exhausts, etc.). Thus, total emissions were probably several times larger than the TRI data indicate.

Following emission, organics are dispersed widely in the environment. Long-distance transport occurs primarily in runoff, groundwater, and the atmosphere (Cohen, 1986). The latter pathway has spread organics to the most remote regions of the globe (Schroeder and Lane, 1988). Chlorinated pesticides such as DDT, lindane, dieldrin, and hexachlorobenzene (HCB) are the best-known examples, having been detected in inorganic media and organisms as distant from emissions as the Arctic and Antarctic (Atlas and Giam, 1981; Tanabe et al., 1983; Gregor and Gummer, 1989). Long-distance dispersal of nonpesticide organics, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorophenols, and alkanes, has also been demonstrated (Lunde and Bjorseth, 1977; Helt et al., 1984; Paasivirta et al., 1985; Wickstrom and Tolonen, 1987; Gregor and Gummer, 1989).

What are the consequences of this global organic contaminant load on the structure and function of organisms and natural ecosystems?

PROBLEM STATEMENT

A vast amount of literature has been accumulated on the ecotoxicology of organics in natural environments. However, it is quite clear that the driving force for research has been the concern over their accumulation in crops for human or livestock consumption, primarily as residues following pesticide applications, and in accumulation via biomagnification up aquatic and terrestrial food chains to organisms that are consumed by humans (e.g., fish), or organisms that bring us aesthetic pleasure (e.g., birds). There is, comparatively, a severe dearth of information concerning the fate and effects of toxic organics in noncrop, terrestrial, vascular plants.

The only comprehensive assessment of the literature on organic chemicals and terrestrial plants is the EPA-funded PHYTOTOX computer database (Fletcher et al., 1988). This database contains 77,825 dose-response (effects) records gleaned from 9,700 bibliographic references published between 1926 and 1984. Of the 1,569 species represented in PHYTOTOX, only 417 are native species growing in natural habitats. The latter value increases to 557 if old-field-succession species are included. Together, wild-grown and old-field species constitute 4,524 records, or 5.8% of the total database. Thus, the existing literature is heavily oriented toward agronomic species. Pesticides constitute 21% of all PHYTOTOX effects records. In fact, of the 20 most often cited chemicals, only two (both hormones) are not pesticides. And, only 4.7% of records are for native plants growing in natural environments.

From the toxicological standpoint alone, it is evident that insufficient data exist for EPA to undertake risk analyses for the effects of organics on natural terrestrial vegetation. In addition, little is known concerning deposition rates of organics to terrestrial ecosystems, rates of plant uptake, and subsequent translocation and metabolism.

The objectives of this report are to: (1) discuss mechanisms of atmospheric deposition of organic substances to terrestrial vegetation; (2) describe probable pathways of terrestrial vascular plant uptake of organics; (3) summarize existing literature on the effects of organics on terrestrial vascular plant growth and physiological processes; (4) speculate on potential, as yet unstudied, effects; and (5) recommend areas for future research.

I rely heavily on the herbicide literature, which greatly exceeds that for all other organics combined, but make no claim to provide any but the most cursory overview. I will consider all kinds of airborne organics, with the exceptions of peroxyacetyl nitrate (PAN), a known gaseous oxidant and phytotoxin that has received much attention during the last 20 years (see Mudd, 1975, for a review), and the chlorofluorocarbons. Also, I will not review the effects of water-borne organics on aquatic macrophytes.

CONCEPTUAL APPROACH

Figure 1 shows a model of the various fluxes of airborne organic substances onto, into, and through terrestrial vascular plants. Fluxes specific to the canopy are shown in detail in Figure 2. In the discussion that follows, I will deal with most of these fluxes, with the exception of within-soil fluxes, which are beyond the scope of this paper. Following that, I will describe known effects of organics on terrestrial plants, and finish with recommendations for future research.

ATMOSPHERIC DEPOSITION

Atmospheric Occurrence

Organics enter the atmosphere primarily in gaseous or particulate form. Initial mixing in the air leads to partitioning between the vapor, solid, and liquid phases (Schroeder and Lane, 1988). Phase distributions are determined by inherent chemical properties, including vapor pressures, Henry's Law constants (H, equilibrium ratio of the concentration in air to concentration in water), diffusion coefficients in air and water, and equilibrium constants (pK_a; for weak acids) (Tucker and Preston, 1984; Mackay et al., 1986; Bidleman, 1988; Ligocki and Pankow, 1989). Organics enter precipitation by dissolving directly from the vapor phase into water droplets and by being physically scavenged as aerosols by falling droplets. The "washout ratio" (W; mass of organics per unit volume of rain divided by mass of organics per unit volume of air) describes the net effect of these processes (Bidleman, 1988).

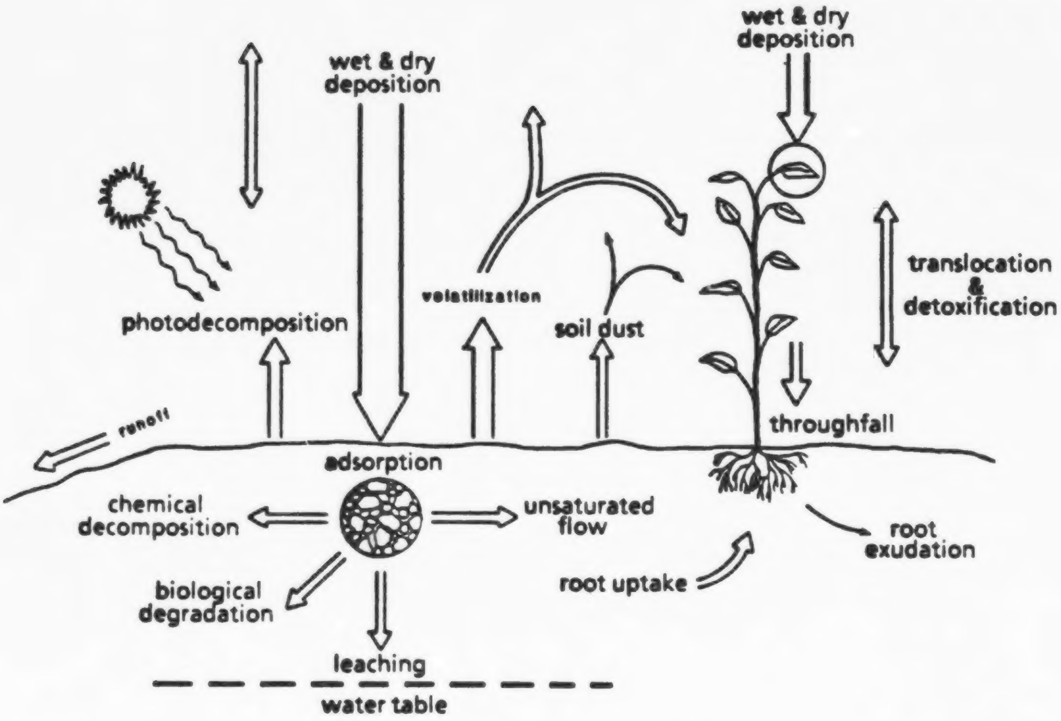
wet & dry deposition
wet & dry deposition
photodecomposition
volatilization
soil dust
translocation & detoxification
runoff
throughfall
adsorption
chemical decomposition
unsaturated flow
root exudation
root uptake
biological degradation
leaching
water table

FIGURE 1. Conceptual model of fluxes of airborne organics to and within terrestrial ecosystems.

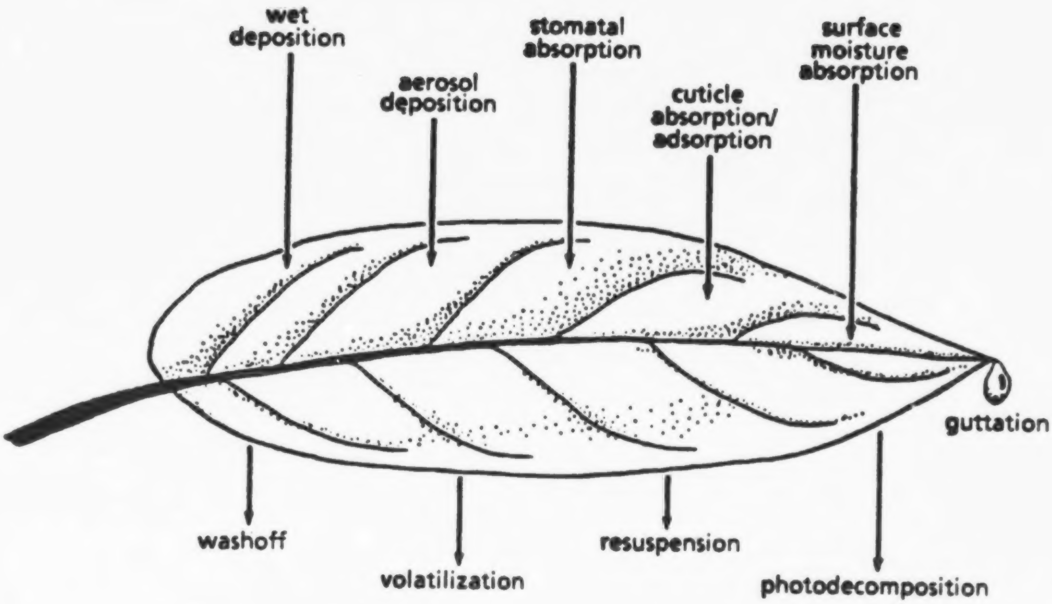
wet deposition
aerosol deposition
stomatal absorption
cuticle absorption/ adsorption
surface moisture absorption
guttation
washoff
volatilization
resuspension
photodecomposition

FIGURE 2. Same as Fig. 1, but enlarged to show fluxes associated with leaves.

Compared to the major air pollutants (ozone, sulfur dioxide, nitrogen dioxide, carbon monoxide), air concentrations of organics are not well-characterized. A great variety have been detected whenever and wherever they have been looked for. Urban air contains hundreds of volatile organic compounds (VOCs) from industrial emissions, motor vehicle exhausts, and other anthropogenic sources (Atlas and Giam, 1988; Bruckmann et al., 1988; Shah and Singh, 1988; Edgerton et al., 1989). Some VOCs are secondary products of the photochemical reactions that produce smog (e.g., nitrophenols [Nojima and Kanno, 1977]). These VOCs are transported downwind to rural regions (Rice et al., 1986; Rippen et al., 1987; Shah and Singh, 1988; Schroeder and Lane, 1988). Reverse transport also occurs; although having highest concentrations in agricultural areas, chlorinated pesticides are regularly found in urban air (Abbott et al., 1966; Stanley et al., 1971; Kaushik et al., 1987; Bruckmann et al., 1988). Natural vegetation, especially trees, puts out substantial quantities of VOCs, primarily monoterpenes, which mix with anthropogenic VOCs (Roberts et al., 1985; Trainer et al., 1987; Kreuzig et al., 1988; Petersson, 1988). Table 1 summarizes the range of concentrations of selected organics measured in air and rain.

TABLE 1. CONCENTRATIONS OF SOME PESTICIDES, PCBS, PAHS AND OTHER VOLATILE ORGANIC COMPOUNDS IN AIR AND WATER, UNITED STATES[a]

Compound	Air (ng/m^3)	Rain (ng/L)
Hexachlorobenzene	0.13-0.29	0.40-1.0
α-/γ-HCH	0.30-5.4	6.4-37
DDT/DDE	0.02-0.33	0.50-4.3
Chlordane	0.04-1.3	trace-2.3
Dieldrin	0.02-0.08	0.8-2.0
Toxaphene	0.6-13.1	7.31-59
PCBs	0.06-9.3	0.10-200
Pthalate esters	1.0-290	>200
Benzo(a)pyrene	1.3-500	2.2-7.3
Formaldehyde	2375-12250[b]	<0.01-1.1
Acetaldehyde	0-9900[b]	<0.04-1.1
Benzene	1950-10700[b]	-[c]
Phenol	39-430[b]	<10-14000
Benzo(a)pyrene	0.01-61	-

[a] Sources: Pearson (1982), Nriagu and Simmons (1984), Giam et al. (1984), Chapman et al. (1986), Atlas and Giam (1988), Shah and Singh (1988), Leuenberger et al. (1988), Duinker and Bouchertall (1989), Sawicki et al. (1960)

[b] lower/upper quartiles

[c] no data available

Wet Deposition

The flux of organics to terrestrial ecosystems in precipitation is simply the volume-weighted product of the concentration in solution and precipitation volume, summed over the time period of interest. A growing literature reports concentrations of organic compounds in rain. Most regularly and widely detected are organic acids, especially aldehydes such as formate and acetate (Chapman et al., 1986 and references therein; Gaffney et al., 1987). Chlorinated pesticides, PCBs, phenols, and n-alkanes have all been reported in rain (Eisenreich et al., 1981; Farmer and Wade, 1986; Agarwal et al., 1987; Gaffney et al., 1987; Jones et al., 1989; Leuenberger et al., 1988; Atlas and Giam, 1988).

Few estimates of wet deposition flux for organics exist. Farmer and Wade (1986) observed 22 to 670 μg/m2/day for C_{12}- C_{32} hydrocarbon fluxes at Norfolk, VA. An estimate for bulk precipitation, which incorporates some aerosols, was 40 and 20 μg/m^2/y for PCBs and lindane, respectively, at Paris, France (Chevreuil et al., 1989). Precipitation falling onto the Great Lakes has been analyzed for PCBs and pesticides for some years. Deposition rates are 0.6 to 9.6 μg/m^2/y for chlorinated hydrocarbons, 424 μg/m^2/y for PAHs, and 120 μg/m^2/y for PCBs (Nriagu and Simmons, 1984).

Dry Deposition

Dry deposition of atmospheric substances onto natural vegetation is described by the equation

$$F = C_a * V_d$$

where F = flux density, C_a = atmospheric concentration at a reference height above the vegetation, and V_d = deposition velocity. Deposition velocity has four components:

$$V_d = 1/(r_a + r_b + r_s + r_c)$$

where r_a = bulk aerodynamic resistance, r_b = leaf or soil boundary layer resistance, r_s = stomatal resistance, and r_c = chemical resistance.

Aerodynamic resistance represents the turbulent downward movement of parcels of air, carrying entrained gases and particles. It is affected by wind speed, the surface area, and vertical distribution of canopy components (foliage, branches, etc.). Boundary layer resistances are related to wind speed and wind direction, and to collecting surface size and geometry. Stomatal resistance is directly proportional to stomatal aperture, which is under physiological control by plants. Chemical resistance comes into play when the concentration of the compound at the absorbing surface is not zero (i.e., it is not quantitatively destroyed or sequestered upon deposition). In this case, the concentration gradient driving flux will be less than C_a.

Deposition of gaseous organics occurs primarily to dry soil and vegetation surfaces and is controlled largely by solubility in the waxy cuticles of plant surfaces and vapor-soil particle partitioning. Absorption of gaseous organics into water is important to wet soils, on plant surfaces following rain or during fog and dew events, in permanent wetlands, and in riparian areas during flooding. Deposition of organics in aerosol form is achieved by the same mechanisms as for aerosols in general: sedimentation, diffusion, and impaction. Sedimentation is most important for large aerosols, diffusion for small aerosols, and impaction for intermediate-sized aerosols (Garland et al., 1988).

Dry deposition of organics has been measured directly by accumulation on surrogate surfaces, including silicon oil-coated nylon screens (Sodergren, 1972); glass plates sprayed with mineral oil or water (McClure and Lagrange, 1977; Murphy, 1984); stainless steel funnels and sinks (Farmer and Wade, 1986; Chevreuil et al., 1989); and pans filled with water, ethylene glycol-water, or glycerin-water (Bidleman and Christensen, 1979; Christensen et al., 1979). Observed fluxes have been in the range 10^{-3} to 10^{2} $\mu g/m^2$/day for PCBs and various pesticides, yielding V_d values of less than 0.01 to more than 5 cm/s. Confidence in these fluxes is not high because the efficiency collection of surrogate surfaces may vary substantially from that of natural surfaces. Bidleman and Christensen (1979) found that V_d for PCBs, chlordane, and DDT varied geographically and by one to two orders of magnitude from day-to-day. In addition, aerosol and gaseous deposition cannot be distinguished, and volatilization of adsorbed gases is not accounted for. Deposition velocities measured by accumulation have been used to infer dry deposition to the Great Lakes from known concentrations of organics in air (Eisenreich et al., 1981).

Fogs, Clouds, and Dew

Cloud water and fog water contain higher concentrations of organic acids and much higher concentrations of pesticides than does rain (Glotfelty et al., 1987; Igawa et al., 1989; Munger et al., 1989; Schaefer et al., 1989). Organic acids have also been reported from dew (Mulawa et al., 1986).

Interception of cloud water and of advective (seacoast) fog water is modeled as a dry deposition process, with cloud and fog droplets acting like large aerosols (Lovett, 1984). Deposition of radiation (valley) fog water is similar to precipitation (i.e., gravitational settling of water droplets). Dews form by condensation of water vapor onto surfaces whose temperature drops to the dewpoint;

deposition rates can be predicted using the Penman-Monteith equation. Organics enter dews by gaseous absorption and aerosol sedimentation. There appear to be no deposition estimates for organics in fogs, clouds, and dews.

Total Atmospheric Deposition

Accumulation rates of persistent (slow to degrade) organics in sediments yield an estimate of net atmospheric deposition (i.e., not accounting for volatilization). For example, Heit et al. (1981, 1988) and Gschwend and Hites (1981) measured PAHs in lacustrine and marine sediment cores in the northeastern United States. Fluxes in recent decades ranged from 36 to 4,870 $\mu g/m^2/y$, with greater fluxes near urban areas. Jones et al., (1989) measured PAHs in archived, dry soil samples collected since 1843 in rural England. Mean deposition rates (1880-1980) were 4,560 $\mu g/m^2/y$. Wickstrom and Tolonen (1987) found that PAH fluxes into sediments of small Finnish lakes had increased substantially since the early nineteenth century.

Swackhamer and Armstrong (1986) estimated net atmospheric deposition of 2 $\mu g/m^2/y$ of PCBs in recent decades to several small seepage lakes in Wisconsin. Rapaport and Eisenreich (1988) measured PCBs, HCB, DDT, and toxaphene accumulation in peat bog sediments. Maximum deposition rates in the eastern United States occurred between 1960 and 1978, with reduced rates since 1980.

The only estimate that could be found for recent atmospheric deposition of an organic to a terrestrial ecosystem was that of Matzner (1984) for German beech and spruce forests. Assuming no root uptake or exchange between surface deposits and canopy tissues, he estimated total PAH fluxes of 0.25 to 0.69 $\mu g/m^2/y$.

A regional application of mass balance was applied to the Great Lakes by the International Joint Commission (summarized in Elder et al., 1988). Measurements of PCBs and pesticide concentrations in dated sediments yielded values for long-term inputs. When known contributions of tributaries, runoff, and point sources were subtracted from these values, and outflows added, the difference was ascribable to atmospheric deposition. The atmosphere accounts for 60% of PCB inputs and 78% of benzo[a]pyrene inputs to the Great Lakes.

FLUXES OUTSIDE OF PLANTS

Fates in Soil

Once deposited, the disappearance of organics in soils usually follows first-order kinetics, provided no additional input occurs, and plant uptake is either constant or absent (Ryan et al., 1988). Factors contributing to the disappearance of organics include volatilization, photodecomposition, adsorption to soil particles, chemical and biological (microbial) degradation, unsaturated and saturated flow, and leaching to deeper soil layers (Figure 1). Consideration of these processes (except volatilization) is beyond the scope of this paper. However, modeling of disappearance rates is useful in determining the likelihood of organics to accumulate to concentrations at which plant root uptake will become significant (Ryan et al., 1988).

Volatilization

In general, volatilization rates of organics from plant canopies increase with increasing vapor pressures and decreasing Henry's law constants (H). Foliar volatilization rates do not fit simple first-order kinetics because of diurnal variability in environmental conditions (solar radiation, wind speed, etc.), and plant uptake (Willis et al., 1986). There is no simple relationship between volatilization rates of organics from soils and either vapor pressure or H values; such factors as adsorption coefficients to soil particles and soil moisture content are also important (Kilzer et al., 1979; Mackay et al., 1986; Spencer et al., 1988). Measured volatilization losses of herbicides in agricultural fields show great variability; 4.5% per year for dieldrin, but less than 1% per year for carbofuran (Caro et al., 1976); 80% per year for PCBs (Moza et al., 1979); 8, 24, and 34% over a six-day period for toxaphene, parathion, and fenvalerate, respectively (Willis et al., 1986); less than 1% over seven days for diclofop (Smith et al., 1986); and 21% over five days for 2,4-D (Grover et al., 1985).

A substantial proportion of herbicides volatilized from soils can be redeposited on crop canopies, especially DDT, PCBs, and the nitrophenol dinoseb (Parker, 1966; Prendeville, 1968; Beall and Nash, 1971; Kaufman, 1976; Moza et al., 1979; Fries and Marrow, 1981; Bacci and Gaggi, 1985). Topp et al. (1986) found that the proportion of soil-applied organic chemical uptake by barley foliage increased as the volatilized fraction of applied chemical increased.

Wash-Off and Resuspension

Wash-off occurs when rain physically dislodges particles or carries away dissolved gases and particulates from plant surfaces; these are then deposited to the soil in throughfall (Figures 1 and 2). The highest proportion of wash-off to amount applied is for pesticides with high solubility in water, for those applied in particulate form, and when heavy or repeated rains occur shortly after application. Time-course studies of individual rain events reveal that wash-off is rapid at first, then diminishes asymptotically toward zero. Wash-off increases with increasing rain amount, up to some saturating intensity (Isensee and Jones, 1971; Steffens and Weineke, 1975; Cohen and Steinmetz, 1986; Willis et al., 1986).

Resuspension is the reentrainment of particles deposited on plant surfaces in moving air (Figure 2). Particle adhesion and windspeed are the primary factors influencing this process (Nicholson, 1988). Soil particles may be entrained in the atmosphere (wind erosion) or ejected into the air by raindrop splash (Chamberlain, 1975), from whence they may be redeposited on plant surfaces (Pinder and McLeod, 1988).

FLUXES INVOLVING PLANTS

Organics must penetrate plant tissues before they can exert physiological effects. Thus, aerosol deposition and nonstomatal deposition of gases are appropriately considered as separate processes from plant uptake. In the case of stomatal absorption, deposition and uptake are equivalent because the sink is the mesophyll.

Uptake rates are determined by external concentration, concentration in plant tissues, and resistances to uptake. For shoots, the most important physical barrier is the cuticle. For roots, the cell membranes of the endodermis are a significant barrier. Following uptake, if the substance is not translocated or metabolized to other forms, it may accumulate in tissues, reducing the concentration gradient across the plant surface, and thus reducing flux. Translocation to other parts of the plant, or metabolic conversion to other compounds, will lower internal concentration near the sites of uptake, maintaining the concentration gradient.

Foliar Uptake of Vapor-Phase Organics

Radioisotope studies with carbon-14 (^{14}C) labeled organics have demonstrated that in most plant species, uptake of PCBs is primarily by leaf vapor absorption, even when the PCBs are applied to the soil (Nash and Beall, 1970; Iwata and Gunther, 1976; Weber and Mrozek, 1979; Bacci and Gaggi, 1985). Nash and Beall (1970) and Beall and Nash (1971) found the same to be true of soybean plants exposed to soil-applied DDT, but soil volatilization was less important for dieldrin, aldrin, and heptachlor. PCBs accumulate in both herbaceous and woody species in proportion to PCB concentration in the surrounding atmosphere (Buckley, 1982). Soybeans absorbed ^{14}C-anthracene vapors from air (Edwards et al., 1982). Accumulation of PCBs, DDT, penta-chlorophenol (PCP), nitrophenols, dioxins, furans, and α-hexachlorocyclohexane (α-HCH) also occurs in conifer foliage (Eriksson et al., 1989; Hinkel et al., 1989, Reischl et al., 1989a).

Gaseous hydrocarbons are readily absorbed by plant foliage. When tomato, barley, and carrot plants were exposed to hydrocarbon vapors (2×10^{-4} M), foliar damage symptoms appeared rapidly (Currier, 1951; Currier and Peoples, 1954). Frank and Frank (1989) exposed Norway spruce saplings to tetrachloroethene in glass chambers. The concentration of tetrachloroethene in the needles (C_n) increased linearly with increasing concentration in the chamber air. At $C_n < 5\ \mu g/cm^3$, the partitioning between air and needles was greater than when $C_n > 10\ \mu g/cm^3$, suggesting surface adsorption, followed by cuticular absorption when adsorption capacity was saturated.

Wolverton et al. (1984) reported that house plants absorbed formaldehyde from the air. However, additional experiments by Godish and Guindon (1989) established that the absorption was by potting soil rather than the plants. Bioconcentration of vapor-phase organics in leaves is closely correlated with their octanol-water partition coefficients [(K_{ow} (Figure 3); Travis and Hattemer-Frey, 1988; Reischl et al., 1989b].

Foliar Uptake of Liquid-Phase Organics

Penetration of the cuticle by herbicides applied in solutions is positively related to their K_{ow} values (Shafer and Schonherr, 1985) and is usually linearly related to herbicide concentration (Bukovac, 1976). Uptake is generally greater to adaxial than to abaxial leaf surfaces, apparently because of the higher density of stomata and greater pubescence that occur on adaxial surfaces (Sargent and Blackman, 1962; Bukovac, 1976). Trichome bases and guard cells are preferred locations of uptake. Mass movement through stomata occurs if the organic, or its solvent, are lipophilic and have low surface tension (Baker, 1970; Bukovac, 1976). Most studies of foliar liquid uptake by herbicides, using ^{14}C labeling, have found substantial uptake (Bukovac, 1976; Steffens and Wieneke, 1975; van Auken and Hulse, 1979), but 2,4-dichlorophenol and dioxin do not appear to penetrate the cuticle (Isensee and Jones, 1971).

When Currier (1951) and Currier and Peoples (1954) exposed plants to pure hydrocarbon liquids, development of foliar damage was rapid, implying fast uptake across the cuticle. In a literature review on hydrocarbon oil effects on plants, Baker (1970) concluded that those oils containing mostly small-molecule, low-volatility hydrocarbons with low viscosity are most phytotoxic; the hydrocarbon constituents readily diffuse across cuticles and cell membranes, evaporative losses are low when applied to soils or foliage, and penetration through stomata occurs.

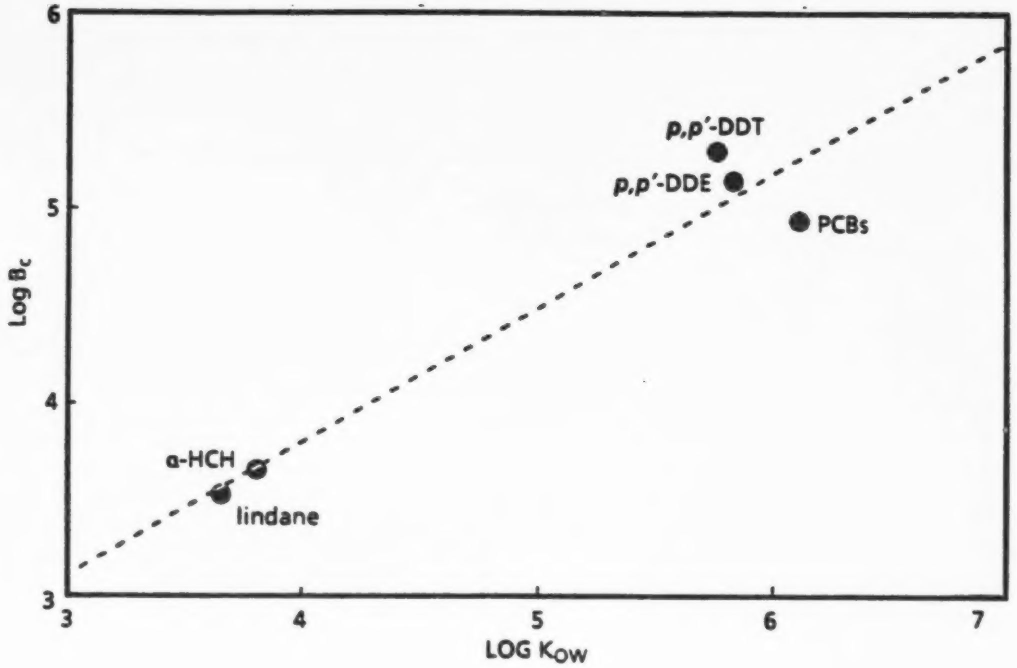

FIGURE 3. The relationship between bioconcentration of organics in plant tissues (B_c; ratio of concentration in plant to concentration in air) and the octanol-water partition coefficient (K_{ow}) (after Travis and Hattemer-Frey, 1988).

Foliar Uptake of Solid-Phase Organics

Organics are frequently adsorbed to the surfaces of atmospheric aerosols, but no studies of particle-associated organic uptake by plants have been conducted. However, cuticular absorption of lipophilic organics is probably much faster from the vapor phase than from the solid phase (Reischl et al., 1989b).

Root Uptake

Many different herbicides are absorbed by the roots of crop plants (Lichtenstein and Schultz, 1965; Lichtenstein et al., 1967; Shone and Wood 1974; Bukovac 1976; Hilton et al., 1976; Briggs et al., 1982; Wickliff et al., 1984; McFarlane and Wickliff, 1985; Scheunert et al., 1986; Topp et al., 1986; McFarlane et al. 1987a,b). A linear relationship is often observed between soil or growth solution concentrations and rates of uptake, at least when concentrations are low. At higher concentrations, uptake may be saturated or even reduced (Fletcher et al., 1990), perhaps due to direct toxicity to the roots. If the original herbicide is not very soluble, root uptake rates may instead be related to concentrations of soluble soil metabolites (Scheunert et al., 1986).

Root uptake has been documented for the insecticides dieldrin, endrin, aldrin, and lindane, but does not occur for DDT and heptachlor (Harris and Sans, 1967; Lichtenstein et al., 1967; Nash et al., 1970). Root uptake has also been observed for dioxins, benzene and substituted benzenes, phenol and substituted phenols, ethanol, naphthol, acetate, tiaryl phosphate esters, pthalate esters, organoborates, and trinitrotoluene (Harley and Beevers, 1963; Isensee and Jones, 1971; Kaufman, 1976; Suzuki et al., 1977; Moza et al., 1979; Mrozek and Leidy, 1981; Shea et al., 1982; Edwards, 1983, 1986; Casterline et al., 1985; McFarlane and Wickliff, 1985; Scheunert et al., 1985, 1986, 1989; Facchetti et al., 1986; Palazzo and Leggett, 1986; Sacchi et al., 1986; Topp et al., 1986; McFarlane et al., 1987a,b; Adriano et al., 1988; Aranda et al., 1989; Krstich and Schwarz, 1989; Fletcher et al., 1990; McFarlane et al., 1990; O'Connor et al., 1990). Depending on the species, plant roots may or may not absorb PCBs and PAHs (Edwards 1983, 1986; O'Connor et al., 1990).

During root uptake, organics move by diffusion in the apoplastic water of the cortex; then, at the Casparian strip, cross the cell membranes of the endodermis to reach the xylem. Shone and Wood (1974), Briggs et al. (1982, 1983), Topp et al. (1986), and McCrady et al. (1987) found a positive, log-linear relationship between the root concentration factor (RCF; ratio of root tissue concentration to external solution concentration) and K_{ow} for various organics. However, in a comparison of nitrobenzene absorption by eight plant species, RCF varied considerably around the predicted value from Briggs et al. (1982), emphasizing the importance of species-specific characteristics (McFarlane et al., 1990).

Bark Uptake

Penetration of the bark of woody plants by herbicides has been reported (Bukovac, 1976). Meredith and Hites (1987) found a variety of PCB congeners in the bark of black walnut and tulip-poplar trees growing near a PCB-contaminated landfill. Very low PCB concentrations in the wood, much higher PCB concentrations in inner than in outer bark, and a positive correlation between congener K_{ow} and accumulation in outer bark suggested that uptake occurred from the atmosphere into the suberin of cork cells.

Translocation

When ^{14}C-labeled herbicides are taken up by roots, most move upward in the transpiration stream, but some remain in the cortex, apparently unable to cross the endodermis (Hay, 1976; Hilton et al., 1976). The proportion translocated varies according to length of exposure, plant species, and type of herbicide (McFarlane et al., 1987b). What is translocated may be found fairly uniformly in all the leaves or may be concentrated in young leaves and growing tips (Hay, 1976). Dry soils reduce rates of translocation, presumably due to lesser transpiration and a lower carbohydrate supply for phloem transport.

Translocation of root-absorbed, non-herbicide organics has been demonstrated for aldrin, lindane, bromacil, triaryl phosphate esters, phenol and chlorophenols, dioxins, pthalate esters, PCBs, trinitrotoluene, and nitrobenzenes (Lichtenstein et al., 1967; Isensee and Jones, 1971; Mrozek and Leigy, 1981; Shea et al., 1982; Casterline et al., 1985; Edwards, 1986; Palazzo and Leggett, 1986; Sacchi et al., 1986; McFarlane et al., 1987a,b, 1990; Aranda et al., 1989; Fletcher et al., 1990). Root- and leaf-absorbed hydrocarbon oils are transported acropetally and basipetally, respectively (Buckley, 1982). However, there is little translocation of root-absorbed PCBs, PAHs, and substituted phenols (Hilton et al., 1976; Kaufman, 1976; Dörr, 1970; Buckley, 1982; Scheunert et al., 1989), nor do root- or leaf-absorbed dioxins and furans appear to be translocated (Reischl et al., 1989b).

There is considerable evidence for a positive relationship between transpiration rate and root uptake (see Figure 4) (Bukovac, 1976; van Oorschot, 1976; McFarlane et al., 1987b). However, Shone and Wood (1976) discovered that neither external concentration nor transpiration rate had much effect on uptake and translocation of triazine herbicides by radish.

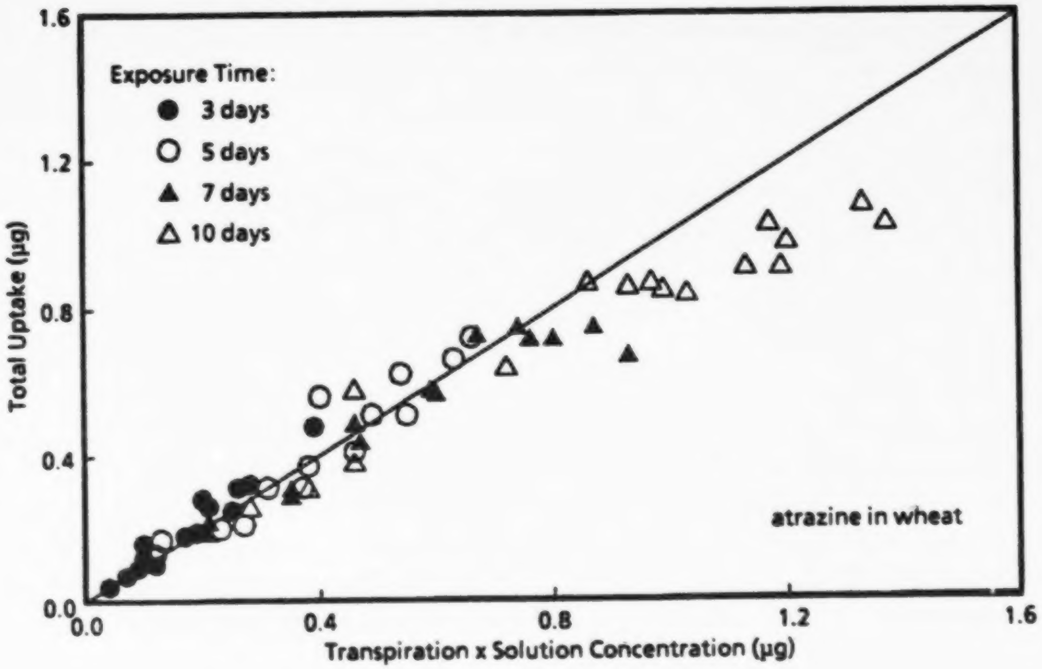

FIGURE 4. The relationship between total uptake of atrazine from solution by wheat and the expected uptake by mass flow through the xylem (after Walker, 1972).

Briggs et al. (1983) observed a positive, log-linear relationship between stem concentration factor (SCF; calculated in same way as RCF) and herbicide K_{ow}. It required 24 to 48 h for SCF to stabilize, with longer equilibration times for higher K_{ow}. They postulated that stable SCF represented abalance between upward transport of root-absorbed compounds and their absorption or degradation by stem tissues.

The herbicide transpiration stream concentration factor (TSCF; ratio of concentration in transpiration stream to concentration in external solution) in barley plants was usually less than unity, implying passive uptake of most herbicides, but greater than unity for 2,4-D, implying active uptake (Shone et al., 1973; Shone and Wood, 1974). The nitrobenzene TSCF was consistently less than one in eight plant species (McFarlane et al., 1990). The TSCF was not related in any obvious way to RCF. However, Shone et al. (1974) demonstrated that the TSCF was correlated with the most readily diffusible herbicide fraction in barley roots eluted with water following a period of root uptake. This fraction consisted of the most lipophilic (high K_{ow}) herbicides.

Briggs et al. (1982) observed a bell-shaped relationship between TSCF and K_{ow} in barley (Figure 5). They hypothesized that for $K_{ow} < 1.8$, transport is limited by diffusion across the endodermal membrane; whereas, for $K_{ow} > 1.8$, transport is limited by the rate of transport from the roots to the tops. McCrady et al. (1987) demonstrated that sorption to the xylem tissue was the main limitation on transport rates of organics through excised soybean stems. McFarlane et al. (1987b) found differential root uptake and translocation to the shoot of soybean by bromacil, nitrobenzene, and phenol, although the three chemicals have similar K_{ow} values. Given the scatter in Briggs et al. (1982) relationship, this result is not surprising. Boersma et al. (1988) have developed a model of organic compound transport in the xylem and phloem. This model is most sensitive to K_{ow}, rates of detoxification, membrane permeability, and the volume of xylem and phloem in various organs.

Generally, the bulk of foliar-applied organics is not translocated; that portion that is partitioned to the stem, little goes to the roots (Hay, 1976; Shone and Wood, 1976; Weber and Mrozek, 1979). Foliar-applied ureas, triazines, DNOC, PCP, and hexachlorophene are not translocated (Fogg, 1948; Hay, 1976; Kaufman, 1976; van Auken and Hulse, 1979).

Detoxification

Plants detoxify herbicides primarily by metabolic degradation and to a lesser extent by adsorption to biomolecules. Adsorption to lecithin and cell membranes has been demonstrated for 2,4-D and 2,4,5-T (Wain and Smith, 1976). The metabolic fates of many different herbicides have been elucidated by ^{14}C labeling studies (Naylor, 1976). In most cases, metabolism converts the

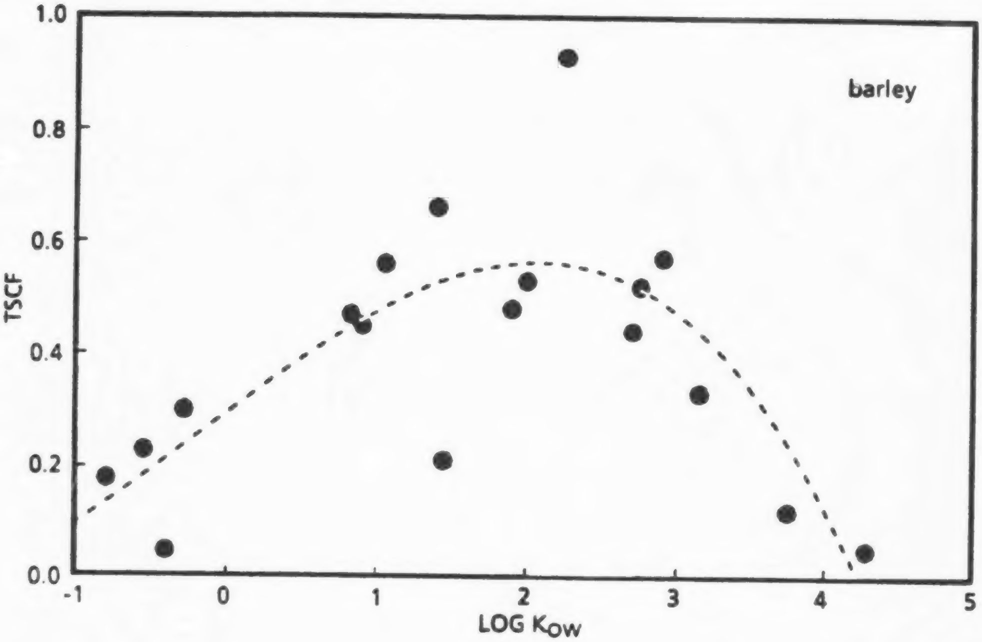

FIGURE 5. The relationship between transpiration stream concentration factor (TSCF; ratio of concentration in transpiration stream:concentration in nutrient solution) of various organics and octanol-water partition coefficients (K_{ow}) in barley (after Briggs et al., 1982).

phytotoxic herbicide to nonphytotoxic or less phytotoxic forms; however, the reverse is sometimes true (e.g., amitrole, bipyridyliums, 2,4-D precursors, DNOC esters) (Wain and Smith, 1976; Menn and Still, 1977). Generally, detoxification proceeds in two steps: (1) an oxidizing, reducing, or hydrolyzing reaction that modifies the organic toxin by adding reactive groups; and (2) a subsequent conjugation reaction that further reduces toxicity and yields a metabolite in a form suitable for storage or transport (Kaufman, 1976; Menn and Still, 1977).

The metabolic fates of most nonherbicide organics in plants are not well understood. Degradation of PAHs, pthalate esters, 4-nitrophenol dichlorobiphenyls, nitrobenzenes and trinitrotoluene have been reported (Dörr, 1970; Moza et al., 1979; Edwards, 1986; Palazzo and Leggett, 1986; McFarlane et al., 1987a, 1990; Fletcher et al., 1990; Preiss et al., 1989; Schmitzer et al., 1988), but the phytotoxicity of the metabolites is unknown.

One major mechanism of plant detoxification of organics is conjugation to glutathione. For example, corn, sorghum, and sugarcane, which possess this metabolic capability, resist atrazine; whereas broadleaf weeds and grasses, which do not have this capability, are susceptible to atrazine. Schroder and Rennenberg (1989) reported glutathione conjugation of pentachloronitrobenzene (often sprayed on crops to protect them from pathogens), but not of atrazine, by Norway spruce.

Plant Efflux

Efflux of organics from plants occurs in three ways: (1) foliar efflux or "leaching," (2) passive loss by transpiration, and (3) root exudation (Rovira, 1969; Tukey, 1970). Radiocarbon studies have shown that root exudation of herbicides is an energy-requiring process, occurs in the zone of active root elongation, and involves readily translocatable and little-metabolized herbicides (Bukovac, 1976). The extent to which organics taken up by plants may be subsequently lost by foliar efflux apparently has not been studied.

Siddaramappa and Watanabe (1979) exposed rice plants to ^{14}C-carbofuran in nutrient solutions sealed at the root collar to prevent volatilized carbofuran from reaching the leaves. Transpired carbofuran was trapped in ethylene glycol in shoot chambers. Over a 10-day period, 9 to 17% of the absorbed radioactivity was lost via transpiration, apparently carbofuran was carried passively along in xylem water. Higher transpiration rates resulted in more carbofuran recovered from the air. These authors also found significant radioactivity in guttation water. McFarlane et al. (1990) found that 10-40% of not-absorbed ^{14}C-nitrobenzene volatilized from leaves of crops and woody plants.

KNOWN EFFECTS ON PLANTS

Visual Injury and Growth

As with plant uptake, there is a close association between K_{ow} values of organics and their inhibitory effects on plant germination and growth. A good model that fits a wide range of plant data is a nonlinear equation where toxicity increases linearly up to a critical value of K_{ow}, then falls off at higher K_{ow} (Hansch et al., 1989).

Herbicides

The mechanisms by which herbicides influence growth include inhibition of mitosis, inhibition or stimulation of tissue enlargement and elongation, and alteration of patterns of tissue differentiation (Cartwright, 1976). Herbicides may also alter dry mass distribution among plant organs, prevent pollination, and cause abscission of leaves and other plant parts (Addicott, 1976; Ratsch et al., 1986); and, in the case of auxin-like herbicides such as 2,4-D, abnormal growth of various organs (van Andel et al., 1976). Effects may be manifested at all stages of growth from germination to reproduction. For example, Sund and Nomura (1963) observed that some herbicides were most effective in inhibiting germination, others at inhibiting seedling growth, and still others at inhibiting growth of juvenile plants. Several herbicides, including dinoseb, PCP, 2,4-D and 2,4,5-T were inhibitory at two or more of these life stages.

Substituted phenols vary widely in their effects on germination and seedling growth (Sund and Nomura, 1963; Amer and Ali, 1968; Shea et al., 1983). Root growth is stimulated by 2,4-dinitrophenol (DNP) at low concentrations and is inhibited at high concentrations, probably because it is a respiratory uncoupler (Shea et al., 1983). Chlorosis, wilting, and necrosis of peas is caused by 2-nitrophenol and 2,4-dichlorophenol (Amer and Ali, 1968).

Van Haut and Prinz (1979) studied the effects of a number of organic vapors on the growth of several crop species. Over a wide range of concentrations (0.1-7.0 mg m^{-3}), relative growth reductions were positive log-linear for all chemicals and species studied. Growth reductions relative to those caused by sulfur dioxide at equivalent concentrations varied between plant species and were usually higher at lower concentrations. The most phytotoxic substance was ethylene (up to eight times the growth reduction of sulfur dioxide), followed by formaldehyde and acetic acid. Dimethylformamide and methanol were less phytotoxic than sulfur dioxide. Dichloromethane, toluene, trichloroethylene, acetone, and xylene caused little or no growth reduction at concentrations up to 60-160 mg/m^3.

Surfactants are often used to improve "wettability" of foliar-applied herbicides. These substances may in themselves increase, reduce, or have no effect on the growth of crops (Lichtenstein et al., 1967; Singh and Orsenigo, 1984).

Other Organics

Toxicity of pure hydrocarbon sprays applied to plants increases in the order: straight-chain paraffins < napthenes and alkenes < aromatics (Crafts and Reiber, 1948). When barley, tomatoes, and carrots were exposed to hydrocarbon vapors, toxicity increased in the order: benzene < toluene < xylene < trimethylbenzene (Currier, 1951). The symptoms started with increased foliage odor, followed by the appearance of dark areas on the foliage, wilting, and, at higher concentrations, death. Shoot dry mass gain was positively correlated with vapor concentration for sublethal doses. When these same compounds were sprayed on foliage as pure liquids, the same order of toxicity was observed, but the differences among hydrocarbons were greater, apparently because of differences in volatilization (vapor pressure decreasing in reverse order to toxicity). Currier and Peoples (1954) repeated these experiments, finding that toxicity increased in the order: hexene < hexane < cyclohexane < cyclohexene < benzene.

Crude oils, their refined products, and coal liquid cause visual injury and reduce growth of a variety of weed and crop species (Baker, 1970; Blankenship and Larson, 1978; Warner et al., 1984). Toxicity is due to the mixture of hydrocarbons in these liquids, including alkanes, alkenes, napthenes, naphthalenes, phenols, and aromatics. Many hydrocarbons are known to be toxic in the presence of ultraviolet radiation (Larson and Berenbaum, 1988). For example, the PAH fluoranthene causes foliar injury under UV light (Zweig and Nachtigall, 1975). Creosote, a widely used wood preservative, contains a variety of PAHs and other aromatics. Concentrations of 18 to 34 mg/L reduced root growth of onion by 50% (Sundstrom et al., 1986).

Aroclor 1254, a mixture of PCBs, inhibited height growth and fresh mass increase of both soybean shoots and roots; at higher concentrations, newly formed leaves showed abnormal curling (Weber and Mrozek, 1979). Pthalate esters caused reduced growth and chlorosis of new leaves and growing tips of tobacco and corn (Buta, 1975; Shea et al., 1982). Tributyl phosphate reduced root growth of rice, radish, and soybean at concentrations of 10 to 100 μg/g soil (Muir, 1984). Trinitrotoluene (TNT) lowered root and shoot growth of nutsedge (Palazzo and Leggett, 1986). Sodium tetraphenylborate (NaTPB) reduced growth of loblolly pine seedlings because of increased plant boron uptake to toxic levels (Kaplan et al., 1988). NaTPB's major degradation product, diphenylboric acid (DPBA), did not affect growth. However, both NaTPB and DPBA, as well as biphenyl, another breakdown product, reduced growth of sorghum, with NaTPB having the greater influence (Adriano et al., 1988).

Many substituted phenols have auxin-like activity. Harper and Wain (1969) found that the greatest growth promotion in standard auxin activity tests was produced by phenols with substitution at both ortho-positions. Like phenols, PAHs can stimulate plant growth (Gräf and Nowak, 1966). Several alcohols promoted growth of excised wheat roots in the light, whereas others had no effect (Gudjonsdottir and Burstrom, 1962). Hexadecanol and docosanol decreased growth of tobacco (Bourget and Parups, 1963). Organic acids and aromatic alcohols, aldehydes, and carboxylic acids inhibited lettuce germination (Mayer and Evenari, 1953; Reynolds, 1978). The insecticides parathion, diazinon, and lindane significantly reduced root growth, but not shoot growth, of peas; whereas, simazine reduced both root and shoot growth (Lichtenstein et al., 1967). Vapor-phase aldehydes at concentrations > 0.2 ppm caused foliar injury to petunias (Brennan et al., 1964).

Gas Exchange and Water Relations

Herbicides

For most herbicides studied to date, stimulation, inhibition, or no effect on dark respiration have been reported (van Oorschot, 1976). In some cases, lower concentrations stimulate; whereas, higher concentrations inhibit, a typical response for oxidative uncouplers such as DNP (Shea et al., 1983). Respiration may also be affected differentially by the same herbicide in different plant organs.

Inhibition of net photosynthesis has been observed in a wide variety of herbicides when plants are exposed to herbicides in soils or nutrient solutions, or applied to foliage (van Oorschot, 1976). With the exception of acylamides, virtually all herbicides tested to date inhibit net photosynthesis and, when a range of concentrations is studied, inhibition increases with increasing concentration. Unlike respiration, stimulation of net photosynthesis has not been observed (van Oorshot, 1976).

All herbicides that reduce net photosynthesis reduce transpiration as well, such as DNP (Barber and Koontz, 1963; Pemadesa and Korelege; 1977). This phenomenon raises the question as to whether or not photosynthetic inhibition is primarily due to stomatal closure, or to nonstomatal (biochemical) effects. Nonstomatal inhibition can be represented as a "mesophyll resistance" (r_m) in series with r_b and r_s. Imbamba and Moss (1971) found that r_m for CO_2 in corn exposed to atrazine increased without an accompanying change in r_s. Most evidence for the relative roles of r_s vs. r_m is indirect, however. When photosynthesis and transpiration were measured simultaneously following exposure to ureas, triazines, diazines, bipyridyliums, and simeton, the relative reduction in photosynthesis was greater than that of transpiration, and commenced sooner (van Oorshcot, 1976). This suggested direct herbicidal action at the sites of photosynthesis. However, for PMA, DSA, ioxynil, propanil, nitrofen, and fluorodifen, photosynthesis and transpiration were inhibited to a similar extent and at the same time, implying that stomatal closure restricted uptake of CO_2. Similar variations in the relative reduction of transpiration vs. photosynthesis were observed for nitrobenzene (McFarlane et al., 1990). Herbicides also disrupt the water economy of plants by reductions in root water uptake, as reported for phenoxy herbicides, ureas, triazines, propanil, and dinoseb (van Oorschot, 1976).

Herbicides that inhibit the light reactions of photosynthesis often inhibit photorespiration as well. This has been demonstrated by similar reductions in net photosynthesis of wheat and corn in air with normal and low O_2 concentrations following exposure to diuron (Downton and Tregunna, 1968), and by the absence of the postillumination CO_2 burst in barley exposed to atrazine (Imbamba and Moss, 1971). However, when corn was exposed to atrazine, CO_2 evolution in the light was greater than in darkness, suggesting little or no suppression of photorespiration (van Oorschot, 1976).

Other Organics

Organic chemicals other than herbicides have been shown to influence plant growth and development. Wood et al. (1985) and Wood and Payne (1986) found that pecan leaves sprayed with the fungicides propiconazole, benomyl, triphenyltin hydroxide, and dodine, or with pyrethroid, carbamate, and organophosphate insecticides showed inhibition of net photosynthesis of up to 20% within one day following application, with full recovery usually occurring within several days. Hydrocarbon oils universally reduce transpiration and net photosynthesis of crops (Baker, 1970). Recovery of both processes is correlated with the dissipation of foliar-applied oils, and raising the CO_2 concentration of the air reduces inhibition, suggesting that blockage of stomata is the cause of inhibition. However, due to the rapidity with which hydrocarbons penetrate leaf tissues, nonstomatal effects are likely as well. Hydrocarbon oils either increase or decrease respiration, with the effect differing among oils and between plant species (Baker, 1970). Nitrobenzene at 8 g/L in growth solution had varying effects on gas exchange of several species; ranging from no effects on soybean to complete photosynthetic repression of green ash (McFarlane et al., 1990). Even at 100 g/L, nitrobenzene did not affect soybean gas exchange (Fletcher et al., 1990).

One hypothesis to account for European forest-tree decline or "Waldsterben" is phytotoxicity of anthropogenic and biogenic hydrocarbons. When young Norway spruce were exposed to β-pinene vapors, photosynthesis was inhibited and chlorophyll degraded (Gross et al., 1988; Wagner et al., 1989). β-pinene inhibits the Hill reaction (Pauly, 1981), resulting in uncoupling of oxidative phosphorylation (Wagner et al., 1989). Frank and Frank (1985) were able to reproduce the decline symptom of needle yellowing in Norway spruce by exposing branches to vapors of two anthropogenic VOCs, tri- and tetrachloroethene, in the field. They later showed (1986, 1989) that these compounds were absorbed by spruce needles and, in the presence of sunlight, the compounds caused photodegradation of photosynthetic pigments. Rippen et al. (1987) have speculated that nitrophenols injure forests.

Ultrastructure and Membrane Function

Because most organics are lipophilic, it is not surprising that they often disrupt cell membranes. At low concentrations, dissolution of organic molecules in membranes forces apart the fatty acid chains of the phospholipids, increasing membrane permeability. At higher concentrations, the bilayer configuration may disintegrate completely. Some organics disrupt cell membranes indirectly through the formation of free radicals, inhibition of lipid synthesis, or changes in the types of lipids synthesized. The disruption of membranes probably accounts for many of the ultrastructural changes attributed to organics.

Herbicides

Contact foliar damage ("burning" or "wetness") by 2,4-D, endothal, and several other herbicides is believed to result from physical disruption of cell membranes (Morrod, 1976). Paraquat disrupts membranes because its metabolism produces hydrogen peroxide (Morrod, 1976). Two consequences of membrane damage are leakage of cell contents and altered rates of active uptake. For example, DNP increases plant cell permeability to water, whereas stomatal closure caused by atrazine, 2,4-D, and DNP may be caused by leakage of K^+ from guard cells (Morrod, 1976; Shea et al., 1983). Ultrastructural changes induced by herbicides in leaves include swelling of thylakoids and chloroplasts, destruction of phloem and vascular cambium, abnormal differentiation of xylem, bark, and root cells, and mitotic abnormalities (Amer and Ali, 1969; Linck, 1976; Moreland and Hilton, 1976).

Other organics

Despite rather low K_{ow} values, bulky hydrocarbons are effective at disrupting membranes. For example, heptene-2, with a bent configuration, causes discoloration and death of cotton hypocotyls, while straight-chain heptane shows no phytotoxicity (Morrod, 1976). It has also been shown that β-pinene alters the relative proportions of lipids and causes disappearance of microsomes in Norway spruce needles (Frosch et al., 1989; Klingler and Wagner, 1989).

Translocation

Root ion uptake is inhibited by many organics. For example, nitrophenols, 2,4-D, simazine, and propanil inhibit phosphate uptake, DNP inhibits Ca^{2+} uptake, the organophosphorus insecticide Systox inhibits Cl^- uptake, and phenolic acids inhibit phosphate and K^+ uptake (Barber and Koontz, 1963; Glass, 1973, 1974; Oertli and Ahmadi, 1975; Kaufman, 1976; Morrod, 1976). As uptake of these ions is energy-requiring, the mechanism of reduced uptake may be inhibition of respiration or uncoupling of oxidative phosphorylation.

Herbicides alter the qualitative and quantitative nature of solute transport in plants. The major effects are physical obstruction of the phloem caused by unorganized cell division, blockage by callose formation, localized xylem/phloem tissue injury or death, stimulation or inhibition of metabolic sinks, and decreased transpiration (Ashton and Bayer, 1976). The only reference found for a non-herbicide organic was Wedding and Riehl (1958), who reported that petroleum oil inhibited phosphate transport from roots to leaves in lemon seedlings.

Metabolism

Herbicides

Herbicides have various modes of action. Many interfere with mitochondrial metabolism. Chloro- and nitro-phenols, benzimidazoles, nitriles, and phenoxy acids are uncouplers of oxidative phosphorylation (i.e., the synthesis of ATP is stopped even though respiration continues) (Beevers, 1953; Kaufman, 1976; Kirkwood, 1976; Shea et al., 1983). Substituted phenols vary widely in their uncoupling ability (Gaur and Beevers, 1959). Other herbicides, including amides, benzoic acids, carbamates, dinitroanilines, halogenated aliphatics, thiocarbamates, triazines, triazoles, and ureas, reduce oxidative phosphorylation by either inhibiting the transfer of energy to intermediates in the formation of ATP, or inhibiting the flow of electrons along the electron-transport chain (Kirkwood, 1976). Glycolysis is inhibited by halogenated aliphatics and phenoxy acids; the latter also inhibit the pentose-phosphate pathway (Kirkwood, 1976).

Many herbicides negatively affect photosynthesis. Inhibition of electron transport in Photosystems I and II occurs by removal or inactivation of intermediate electron transport carriers, or by the herbicide acting as an electron acceptor in competition with normal acceptors. This inhibition is light-dependent. Uncouplers dissociate electron transport from ATP synthesis (photophosphorylation). Some herbicides are both inhibitors and uncouplers. For a comprehensive review, see Moreland and Hilton (1976).

Herbicide effects on intermediate metabolism are numerous. Many inhibit rates of synthesis or degradation of carbohydrates, lipids, proteins, and nucleic acids, or alter the types of these compounds formed (Cherry, 1976; Kirkwood, 1976; Morrod, 1976). However, 2,4-D and 2,4,5-T stimulate lipid synthesis (Morrod, 1976). Some herbicides inhibit nitrite reduction, causing nitrite to accumulate in plant tissues (Klepper, 1979).

Other Organics

Fungicides (e.g., captan) inhibit respiration and photosynthesis at the cellular level in a similar manner to herbicides (Budimir et al., 1976). Evidence exists for inhibition of gylcolysis, aerobic respiration, and uncoupling of oxidative phosphorylation by hydrocarbon oils (Baker, 1970). Ravanel et al. (1989) reported the uncoupling ability of chlorophenol in maple cell suspensions.

Plant Resistance

Plant species differ in their resistance to herbicide effects, and species sensitivity rankings differ among herbicides. Other factors influencing sensitivity are genotype, growth stage, nutritional status, physical damage, cuticular permeability, temperature, water stress, light intensity, leaf area, leaf morphology, transpiration rate, and rooting depth (Aberg and Stecko, 1976; Muzik, 1976). It is well established that the primary causes of "herbicide selectivity" (the pesticide science term for plant sensitivity) are due primarily to three factors: (1) different rates of uptake by the roots and/or shoots; (2) different rates of translocation and differences in the organs and tissues to which translocation occurs; and (3) different capabilities for, or rates of, metabolic detoxification (Sargent, 1976; Wain and Smith, 1976). At the site(s) of herbicide action, species differences in sensitivity often disappear. For example, the Hill reaction in isolated chloroplasts from different plant species is inhibited to the same degree by the same concentrations of simazine and several other herbicides (van Oorschot, 1976). Differential resistance of plant species to hydrocarbon oils has also been observed (Baker, 1970). In the case of the *Umbelliferae*, cell membranes have inherent high resistance to penetration by oils (van Overbeek and Blondeau, 1954).

It is worth noting that plants contain a bewildering variety of organic compounds that are toxic to animals. Most of these are believed to be evolved, qualitative or quantitative, defenses against herbivory. Interestingly, many of these are known phytotoxins, including organic acids and phenols (Duke, 1977). This fact clearly indicates that many plants already possess mechanisms to detoxify some priority air pollutants.

POTENTIAL EFFECTS ON PLANTS

Ecological Effects

When photosynthesis and respiration are inhibited, or ATP synthesis uncoupled from metabolism, the whole-plant reaction should be reduced growth and reproduction. Energy allocated to alleviating the stress of chronic toxin uptake may also reduce the plants ability to produce defensive chemicals. Inhibition of root water or ion uptake may increase allocation to roots at the expense of shoots. Together, these processes lead to lesser competitive ability of affected species. Except near point sources of toxic organics, these effects may occur gradually as small but continuous atmospheric inputs accumulate. Ultimately, shifts in species composition and dominance may become apparent at the plant community level.

Just which species may suffer most is largely a matter of speculation. For those organics that readily cross the root endodermis, rates of translocation, and hence of bioaccumulation, may be higher for plants with greater transpiration rates (i.e., inherently smaller stomatal resistances). These tend to be early successional species with fast growth rates and among late-successional species that are shade intolerant. Conifers have the highest stomatal resistances of any major plant life form (Korner et al., 1979), yet they also have exceptionally thick, waxy cuticles into which organics may be absorbed. The major route of entry, foliage vs. roots, of organics could play a pivotal role in determining the relative resistances of different plant taxa.

Interactions with other Pollutants

Many organics are weak acids, and their lipophilicity is greater in the unionized form. Penetration of weak-acid herbicides through cuticles increases as solution pH decreases (Fogg, 1948; Sargent and Blackman, 1962; Bukovac, 1976). This phenomenon probably accounts for the enhanced phytotoxicity of nitrophenols and organic acids at low pH (Simon and Beevers, 1951; Simon et al., 1952). As a result, there is a strong possibility that acidified wet deposition increases the phytotoxicity of organics by enhancing uptake (Mullen, 1986).

Biogenic monoterpenes present an interesting case. Like anthropogenic VOCs, they contribute to the photochemical formation of ozone and PAN (Lurmann et al., 1983; Trainer et al., 1987; Chameides et al., 1988) that have been shown unequivocally to reduce photosynthesis and growth of crop and tree species (Reich, 1987). Wagner et al. (1989) have hypothesized that ozone penetrates the mesophyll of conifers, increasing membrane permeability and liberating monoterpenes stored in secretory vesicles. In the presence of ozone, monoterpenes promote the oxidation of sulfur dioxide to sulfate, possibly causing local enhancement of acid deposition to forests (Stangl et al., 1988).

Interactions between different types of gaseous pollutants are well documented (Ormrod, 1982). Because terrestrial plant communities are receiving chronic inputs of possibly hundreds of different organic compounds, it is possible that the overall effects in combination are additive, more than additive, or less than additive.

CONCLUSIONS

Thousands of organic compounds are released into the atmosphere each year by human activities, including pesticides, aliphatic and aromatic hydrocarbons (both halogenated and unhalogenated), polychlorinated biphenyls, and phthalate esters. These are transported long distances and reach natural vegetation via wet and dry deposition. Deposition fluxes and velocities have been characterized for only a few organics in a few geographic areas.

The potential for plant uptake and bioconcentration of organics is high and correlated with octanol-water partition coefficients. Greater transpiration rates produce greater root uptake. Foliar uptake of vapor-phase organics has received little attention. Translocation patterns differ among organic compounds. Metabolic detoxification plays a major role in plant resistance, but has been well characterized only for pesticides.

With few exceptions, the modes of action of organics in plants are well-known only for herbicides. A variety of effects by herbicides, usually but not always inhibitory, have been observed on plant growth and morphology; photosynthesis, respiration, and transpiration; cell membranes and ultrastructure; translocation; and respiratory, photosynthetic, and intermediate metabolism. Many of these same effects have been observed with nonherbicide organics. I found no studies on population-, community-, or ecosystem-level effects of airborne organics.

Relevance of Previous Work

As the analysis of the PHYTOTOX database indicated, there is only one class of organics - herbicides - for which the physiological effects on plants are relatively well known. This is hardly surprising, because their purpose is to kill plants, especially weeds. Although it would be desirable to know more about nonherbicide organics, existing knowledge of herbicide effects is helpful in predicting the impacts of organics in general on terrestrial vegetation. For example, herbicides are at times applied aerially to crops or forests, with consequent downwind drift onto adjacent natural plant communities. Some herbicide precursors (e.g., 2,4-dichlorophenol, used to make 2,4-D, and maleic anhydride, used to synthesize pyridazines) are on the EPA's Toxic Release Inventory (U.S. EPA, 1989). Point releases of these, and of the finished herbicides themselves, from sites of manufacture may affect natural vegetation. A few herbicides have other human sources besides pesticide manufacture and use. For example, DNP, DNOC, and other nitrophenols are produced as by-products of smog-forming reactions. Finally, the observed correlations between plant bioconcentration or modes of action and the physicochemical properties of herbicides permit general predictions to be made concerning the phytotoxic effects of nonherbicide organics.

Nevertheless, the literature emphasis on herbicides poses many obstacles to understanding potential phytotoxicity of airborne organics. One obstacle is that the conditions under which herbicides are applied to plants - high concentrations over short time periods - are quite different from those encountered by natural vegetation - low concentrations in a repeated or continuous manner. Significant differences between acute and chronic exposures to the major airborne pollutants have been demonstrated (Lefohn and Runeckles, 1987). Thus, extrapolation from acute agricultural doses to chronic natural vegetation doses may be unwarranted. Another difficulty is the extremely high concentrations of organics used in most dose-response experiments. For example, solution concentrations of 10^3 to 10^9 ng/L are frequently encountered in phytotoxicity studies. Compare these with the concentrations in Table 1.

The best use that we may be able to make of the existing literature is to rank the likelihood of plant uptake of organics according to the vapor pressures, K_{ow} values, and half-lives in soil of the organics (Ryan et al., 1988; Travis and Hattemer-Frey, 1988).

RECOMMENDATIONS

The most critical areas in need of further knowledge are: (1) spatial and temporal patterns of atmospheric concentrations and wet/dry deposition rates; (2) rates of uptake by roots from soil, and of vapors and wet deposition by shoots; (3) translocation patterns; (4) physiological effects from the whole-plant to the subcellular level; and (5) modes of action. In addition, much more emphasis needs to be placed on nonpesticide organics and on native, nonagricultural species growing in natural environments. In all such work, we must use acute or chronic doses that bridge the range of exposures actually occurring in natural ecosystems.

Some specific suggestions are as follows.

(1) Upgrade routine air, aerosol, and precipitation monitoring networks (e.g., National Atmospheric Deposition Program, National Dry Deposition Network) to measure concentrations of at least the most common and highly concentrated organics.

(2) Characterize dry deposition to various plant communities. Traditional direct measurement techniques - flux-gradient and eddy correlation (Hicks, 1986) - are difficult due to the very low concentrations of most organics. However, new advances in laser technology - FTIR, lidar, tunable diode lasers - hold promise for use of the flux-gradient technique in the near future.

(3) Develop methods to measure short-term uptake of organics by plant shoots. These would complement ^{14}C work by distinguishing between cuticular and stomatal absorption, and would permit scaling-up of leaf-level uptake to entire canopies in inferential methods of estimating dry deposition (Hicks, 1986). The technological challenge of generating and measuring low but stable concentrations is great, but the potential gain in predictive capability should be worth the effort.

(4) Conduct experiments on dose-response relationships of whole plants growing in native soils, including growth, allocation, morphology, water relations, carbon assimilation, and nutrition. Growth chamber, continuously stirred tank reactor (CSTR), and open-top chamber studies, in order, would provide increasing realism in terms of environmental conditions.

(5) Determine the cellular/subcellular modes of action of various classes of organics. Previous work with herbicides suggests that virtually every translocation and metabolic process is worthy of investigation.

(6) Measure dose-response relationships for species representative of other major life forms of terrestrial plants besides crops: annual and biennial weeds, perennial herbs, ferns, evergreen and deciduous shrubs, evergreen and deciduous hardwoods, and conifers.

(7) Develop sensitivity rankings based on absorbed rather than external dose. This approach has yielded better predictive capability for major gaseous air pollutants (Reich, 1987). Because organics vary so widely in their lipophilicity, even within similar structural classes, relationships between external dose and response for one organic are unlikely to apply to other organics.

EFFECTS OF ATMOSPHERIC POLLUTANTS ON PEATLANDS

Noel R. Urban

Environmental Engineering Sciences
Department of Civil and Mineral Engineering
University of Minnesota, Minneapolis, MN

INTRODUCTION

The phenomenon of long-range transport of atmospheric pollutants is well documented. From the Arctic (Murozumi et al., 1969; Weiss et al., 1971; Ng and Patterson, 1981), to the Antarctic (Boutron and Patterson, 1983), and to remote Pacific islands (Atlas and Giam, 1981; Duce et al., 1983), there exists no location on Earth that does not receive measurable atmospheric anthropogenic contaminants. Although humans have been disseminating pollutants through the atmosphere for several thousand years (Patterson, 1980; Kuster et al., 1988), the intensity of air pollution has increased exponentially since the industrial revolution (Edgington and Robbins, 1976; Ferguson and Lee, 1983a) both in terms of the absolute masses of pollutant emissions and the number and type of pollutants (Heit et al., 1981; U.S. EPA, 1989). That air pollutants can cause intense and catastrophic damage to organisms and ecosystems on a local scale is well documented (Gorham and Gordon, 1960a,b, 1963; Gignac and Beckett, 1986). Recent regional declines in forest health have indicated that synergistic effects may occur among pollutants and natural stressors (Schulze, 1989), but our understanding of the effects of chronic exposure to multiple pollutants is very limited.

Peatlands have been considered ideal environments in which to study atmospheric deposition of anthropogenic contaminants. First, peatlands classified as ombrotrophic bogs are isolated from surface and groundwaters, and thus receive all of their hydrologic, nutrient, and mineral inputs from the atmosphere. There is, therefore, no ambiguity about the source of the inputs; substances deposited in bogs were derived from the atmosphere. Second, the continuous accumulation of organic-rich sediments provides an excellent substrate for sorbing metallic and organic pollutants, and sealing them beneath subsequent peat accretions in a fashion that preserves the chronological sequence of deposition. For these reasons, concentrations of S, N, trace metals, major cations, and organic contaminants in surface moss have been used to deduce spatial patterns in atmospheric deposition; and historical changes in deposition of these constituents have been inferred from peat profiles (Mattson and Koutler-Andersson, 1955; Rapaport and Eisenreich, 1986; Norton and Kahl, 1987; Kuster et al., 1988).

The factors that render bogs useful monitors of atmospheric deposition also render them particularly susceptible to damage from atmospheric deposition. The dependence of bog plants on atmospheric supplies of nutrients, trace metals, and major ions implies that changes in atmospheric supply will affect the growth of the bog plants. The situation is exacerbated by the very adaptations of the mosses and lichens to the ombrotrophic conditions. The thin or absent cell walls and the lack of a vascular transport system facilitate the uptake of wet and dry deposition and its associated contaminants (Winner and Atkinson, 1987). The anaerobic, water-logged conditions that cause the rapid sediment accretion also promote acidic, anoxic conditions that enhance the toxicity and persistence of many pollutants reaching this environment. Furthermore, the geographic distribution of peatlands coincides with areas that receive extensive deposition of atmospheric pollutants and further predisposes these sites to damage. Peatlands are prevalent in latitudes north of 40° and thus coincide with major industrial regions in northern Europe and eastern North America (Kivinen and Pakarinen, 1981; Gorham et al., 1987; Matthews and Fung, 1987).

The importance of peatlands as wildlife habitat and vegetation preserves is well known (Karns, 1984; Scoullos and Hatzianestis, 1989). Less well known but of equal or greater importance, are the chemical and hydrologic linkages between peatlands and other ecosystems. Wetlands greatly modify water quality of precipitation and streams by consuming alkalinity (Bayley and Schindler, 1987), sequestering trace metals (Eger et al., 1981) and nutrients (van der Valk et al., 1978), neutralizing mineral acids (Hemond, 1980; Wieder and Lang, 1982), and exporting organic acids (Hemond, 1980; Urban et al., 1989a). Globally, peatlands are significant reservoirs of carbon (Houghton, 1986; Clymo, 1987; Gorham, 1988a), major sources of methane (Matthews and Fung, 1987) and important sources and sinks of S and N gases (Adams and Farwell, 1981; Hemond, 1983; Bowden, 1986a,b, 1987; Nriagu et al., 1987; Urban et al., 1989a,b). Clearly, deleterious effects of atmospheric pollutants on peatlands will have many ramifications extending outside the peatlands themselves.

EVIDENCE OF ATMOSPHERIC TRANSPORT AND DEPOSITION OF POLLUTANTS

There exists a very large body of literature documenting the deposition of atmospheric pollutants in peatlands. A wide variety of pollutants have been examined including components of acid deposition, trace metals, radionuclides, synthetic organic contaminants, soot and magnetic particles from fly ash and dust. Atmospheric deposition has been implicated as the source of pollutants in three different ways. The mere presence of anthropogenic contaminants in remote ombrotrophic bogs constitutes the first piece of evidence implicating atmospheric deposition as the source of contamination. Ombrotrophic bogs receive all hydrologic inputs from the atmosphere; they have no in-flowing streams, receive no groundwater discharge, and receive little or no runoff from surrounding mineral soils. Hence, the only possible source of contaminants found in such sites is the atmosphere. The relatively high radioactivity in mosses in English bogs could only have come from bomb fallout or local emissions to the atmosphere (Gorham, 1958a, 1959). Aerial drift from local use of pesticides has been implicated as responsible for the high burdens of toxaphene in bogs in Maine and Minnesota (Rapaport and Eisenreich, 1986). The presence of pesticides (toxaphene, mirex, endosulfan, dieldrin, chlordane, aldrin, lindane, heptachlor, methoxychlor) and industrial chemicals (polychlorinated biphenyls [PCBs], polycyclic aromatic hydrocarbons [PAHs], and hexachlorobenzene [HCB] in remote bogs in Minnesota, Ontario, and Quebec clearly implicates long-range transport of atmospheric pollutants (Rapaport et al., 1985; McCrea and Wickware, 1986; Rapaport and Eisenreich, 1986, 1988). The existence of untransformed DDT, a compound whose use has been banned in North America for nearly 20 years, in surface peat from sites across northeastern North America can result only from atmospheric transport and deposition of pesticides used in Central America (Rapaport et al., 1985; Rapaport and Eisenreich, 1988).

The second piece of evidence linking atmospheric deposition with the presence of pollutants in peatlands comes from geographic surveys that show correlations between pollutant concentrations in peatlands (surface waters or surface vegetation) and proximity to pollutant emission sources. In a large survey of North American peatlands, Gorham et al. (1985) demonstrated that concentrations of major ions in surface bog waters were controlled by atmospheric deposition of sea spray (Na, Cl, Mg, $SO_4^=$), soil dust (Ca, Mg, Na, K), and air pollutants [($SO_4^=$) see also Urban et al., 1987a]. At these same sites, concentrations of Fe and Al in surface waters also were related to rates of soil dustfall, but concentrations of Pb were explained largely by rates of deposition from anthropogenic sources (Urban et al., 1987b). Similarly, Blancher and McNichol (1987) demonstrated that, compared to peatlands out of the plume, peatlands downwind of the Sudbury smelter (Ontario, Canada) had higher dissolved concentrations of $SO_4^=$, H^+, Ni, Mn, and Cu. Taylor and Crowder (1983) observed that concentrations of Cu, Ni, Fe, and Mg in marsh sediments decreased with increasing distance from smelters. Zoltai (1988) found that concentrations of Zn, Fe, Al, and Pb were elevated in the waters of peatlands within 5 km of a smelter in Manitoba, but concentrations of Zn, Pb, Cu, and As were elevated above background concentrations in peat from sites up to 100 km from the same smelter. Similarly, Gignac and Beckett (1986) observed elevated concentrations of Cu and Ni in bog waters within 5 to 10 km of the Falconbridge smelter (Ontario, Canada) and elevated concentrations in peat up to 30 km from the smelter. Concentrations of $SO_4^=$ and H^+ in English bog waters also increased with proximity to industrial, urban centers (Gorham, 1958b; Gorham and Detenbeck, 1986). Within six months, *Sphagnum* moss transplanted from remote peatland sites in England to bogs near industrial centers showed large increases in concentrations of N, Pb, and Fe in relation to transplants in more remote areas (Ferguson et al., 1984; Woodin et al., 1985) and were attributed to high rates of atmospheric deposition of these elements in the industrial regions. A host of studies have documented correlations between element concentrations in surface moss or peat, and proximity to industrial centers. Concentrations of S in living *Sphagnum* moss and lichens in Finnish peatlands are linearly correlated with rates of S deposition and decrease from south to north (Pakarinen, 1981a). Similarly, elevated concentrations of S, Pb, and Hg were noted in *Sphagnum* from peatlands close to point sources of these pollutants in the maritime provinces of Canada (Percy, 1983; Percy and Borland, 1985). Concentrations of trace metals in surface moss from Finland (Pakarinen and Tolonen, 1976a,b), Canada (Glooschenko and Capobianco, 1978; Percy, 1983; Santelmann and Gorham, 1988), and New England (Furr et al., 1979) have been shown to vary in relation to proximity to industrial or automotive source areas. Similarly, concentrations of ash in peat from Minnesota bogs were found to be highly correlated with distance from agricultural areas (Gorham and Tilton, 1978). The ability of mosses and lichens to accumulate atmospheric pollutants is so well established that they have been used widely as monitors of atmospheric deposition of trace metals (Ruhling and Tyler, 1970, 1984; Pakarinen, 1981b; Folkeson, 1981), synthetic organic chemicals (Thomas and Herrmann, 1980; Thomas, 1983), and radionuclides (Gorham, 1958a; Persson, 1970; Daroczy et al., 1988).

Peat profiles that show correspondence between periods of high rates of accumulation of pollutants and periods of high rates of atmospheric emissions of the pollutant constitute the third type of evidence linking atmospheric deposition with the presence of contaminants in peatlands. Were direct dumping or surface water discharges the source of pollutants to peatlands, different sites would not be expected to show the same historical record of pollutant inputs, and this historical record would not be expected to match the historical pattern of nation-wide or worldwide usage of the chemical. Rapaport and Eisenreich (1986, 1988) have demonstrated that the historical patterns of inputs of DDT, PCBs, toxaphene, HCB, and other pesticides are nearly identical in bogs across northeastern North America; clearly atmospheric deposition is the common source for all of these sites. Similarly, historical records of metal smelting are preserved in Pb profiles within English peat bogs (Lee and Tallis, 1973; Livett et al., 1979). Long-term records of emissions to the atmosphere have been inferred from peat profiles in many locations; for example, Pb in Denmark (Aaby and

Jacobsen, 1979); Pb, Zn, Cu, and magnetic minerals in Canada (Tolonen and Oldfield, 1986; Zoltai, 1988); Pb, Zn, and V in Maine (Norton, 1983; Norton and Kahl, 1987); Pb and Cd in south Germany and Poland (Sapek, 1976; Kuster et al., 1988); and magnetic minerals and trace metals in England, Minnesota, and Finland (Oldfield et al., 1978, 1980; Richardson, 1986). In only a few cases have the accumulation rates of pollutants in peat been compared with independent estimates of atmospheric deposition rates (Norton and Kahl, 1987; Rapaport and Eisenreich, 1988). Thus, it is not clear if the historical deposition record of all pollutants is quantitatively or only qualitatively preserved in peat.

The literature review above is not exhaustive, but it amply documents the deposition of a wide range of atmospheric pollutants in peatlands. The input of atmospheric pollutants including trace metals, radionuclides, synthetic organic chemicals, nutrients, acid deposition, and agricultural and industrial particulates into peatlands near to and far from source areas has been documented throughout North America, Europe, and northern Asia. This large body of literature unequivocally documents that ecosystems throughout North America and Eurasia have been, and continue to be, subjected to inputs of atmospheric pollutants.

EFFECTS OF ATMOSPHERIC POLLUTANTS ON PEATLANDS

Documented Effects

Although numerous effects of air pollutants on peatlands have been documented, the ramifications of these effects are not well known, and it is probable that many existing effects are not yet discovered. The documented effects range from inhibition of enzymes, and declines and disappearance of susceptible species, to changes in such ecosystem functions as nutrient retention, primary productivity and carbon storage. The discussion below of documented and potential effects of air pollutants on peatlands is organized loosely around classes of pollutants including acid deposition, trace metals, radionuclides, and synthetic organic chemicals. Only for acid deposition and trace metals is there adequate documentation of cause and effect. Documentation of cause and effect for other air pollutants has not been determined because of lack of research. The discussion is of necessity condensed, not exhaustive. Additional reviews of this subject may be found in Gorham et al., (1984, 1987) and Gorham (1988a,b).

Acid Deposition

Acid deposition has caused both direct and indirect effects on peatlands. Among the direct effects documented to date are leaching of base cations from peat, inhibition of enzymes, inhibition and stimulation of plant growth, and die-off and disappearance of moss and lichen species. Indirect effects identified at present include changes in hydrology, metal speciation, nutrient retention, and enhancement of erosion.

One adverse effect of acid deposition is the leaching of cations from surface peat. Urban and Bayley (1986) and Bayley et al. (1986, 1987) have documented the increase in base cations in surface bogwaters following experimental spraying of acid to the surface of a bog in the Canadian Experimental Lakes Area. Approximately half of the acid applied to the minerotrophic, marginal area of the peatland was neutralized by ion exchange or leaching of base cations from peat. Skiba et al. (1989) have shown that the base saturation of surface peat throughout Scotland is inversely correlated with rates of acid deposition and the loss of acid-sensitive lichens. They argue that the geographic gradient in acid deposition has caused extensive leaching of base cations and acidification of surface peats in southern Scotland. Bogs are oligotrophic, acidic environments that are vegetated by only the few plant species capable of obtaining nutrients under acidic conditions. The abundance of individuals, and the number of animal species is similarly restricted in these harsh environments (Karns, 1984). In acidic environments the abundance of Ca and Mg is particularly important in blocking the harmful effects of hydrogen ions and aluminum (Mount et al., 1988; Shortle and Smith, 1988). Thus in acidic bogs, leaching of cations from surface peat will further restrict the number of species capable of inhabiting these ecosystems. Reductions in productivity, in rates of decomposition and associated gas release, and in resilience of these species-impoverished systems also may accompany the leaching of cations from bogs. More drastic are the changes likely to occur in poor fens - peatlands with slightly higher pH and base saturation than bogs. Such changes have not been studied yet, and will be discussed below under potential impacts.

Another documented effect of acid deposition on peatlands is the inhibition of plant and bacteria enzyme systems. Press et al. (1985) observed that arylsulfatase activity of peat decreased with increasing proximity to urban industrial centers in England and Wales. The low enzyme activity in peat might be due to a number of components in the peat including sulfur compounds and trace metals. However, peat transplanted to polluted sites and isolated from underlying peat also quickly lost the capacity to cleave arylsulfate esters; this inhibition was reproduced in the laboratory by application of HSO_3^- at concentrations measured in rainfall at these sites (Ferguson and Lee, 1983a). Jarvis et al. (1987) noted a decrease in arylsulfatase activity in surface peat relative to deeper peat from a Virginia peatland. They also attributed the decline in activity in surface peat to inhibition by acidic deposition. Changes in arylsulfatase activity in peat may lead to a number of changes in sulfur cycling including changes in reduced sulfur gas emissions and changes in sulfate reduction and methane production (Yavitt et al., 1987; Giblin and Wieder, 1990). More significantly, they may indicate that other microbial processes have been impacted by acidic deposition.

High rates of sulfur and nitrogen deposition also cause reduced enzyme activity and subsequently reduced growth and loss of sensitive species in peatland vegetation. It has been demonstrated by several studies that high rates of N deposition suppress nitrate-reductase activity and growth rates in *Sphagnum* (Woodin et al., 1985; Press et al., 1986; Rudolph and Voight, 1986; Woodin and Lee, 1987). Although the increasing rates of N deposition in North America appear to stimulate *Sphagnum* growth (Urban et al., 1989b), the much higher rates of N deposition in the Pennine mountain region of England are adequate to inhibit growth of all *Sphagnum* species except *Sphagnum recurvum* (Press and Lee, 1982; Ferguson et al., 1984; Press et al., 1986; Woodin and Lee, 1987). Thus, it is felt that the species composition of English peatlands is determined in part by rates of NO_x emissions.

The deposition of sulfur compounds has had a drastic impact on peatlands in Great Britain and in Canada. The toxicity of SO_2 and HSO_3^- to mosses and lichens (Ferguson et al., 1978; Ferguson and Lee, 1980; Aulio, 1984) has resulted in the disappearance of *Sphagnum* and lichen species from large areas of Great Britain (Tallis, 1964; Ferguson and Lee, 1983b; Lee et al., 1987; Looney and James, 1988). Although emissions of SO_x have declined over the past forty years, combined emissions and toxicity of SO_x and NO_x are sufficient to prevent recolonization by *Sphagnum* (Lee et al., 1987; Woodin and Lee, 1987). Similarly, the combined exposure to SO_2 and trace metals has caused loss of *Sphagnum* from peatlands within a 15-km radius of the metal smelters in Sudbury, Ontario (Gignac and Beckett, 1986). The effects of acidic deposition have not ended with the loss of species. For example, the loss of *Sphagnum* carpets from blanket bogs in England has resulted in accelerated erosion, decreased nutrient and water retention, and enhanced mobilization and toxicity of trace metals (Lee et al., 1987; Helmer et al., 1990). Similarly, loss of *Sphagnum* species has caused lowered water tables, accelerated decomposition and subsidence of peat, and enhanced metal toxicity in peatlands surrounding smelters in Ontario. Acid deposition in Britain provides the best documented example of the susceptibility and potential for widespread damage to peatlands from air pollution. Damage has not been confined to changes in species composition and changes in water quality, but extends to biotic impoverishment of large areas and serious alteration of the functional and structural attributes of the affected peatlands.

Trace Metals

Documented effects of trace metal deposition in peatlands include plant toxicity, amelioration of SO_2 toxicity, and inhibition of enzyme activity in peat. Only five species of vascular plants are capable of growing in peatlands within 2 km of metal smelters in Sudbury, Ontario due to the combined toxicity of Cu, Ni, and SO_2 (Gignac and Beckett, 1986). It is likely that SO_2 is responsible for the elimination of bryophytes within 15 km of these same smelters (Ferguson et al., 1978; Baxter et al., 1989a). However, the altered hydrology within the sites acts to exacerbate the metal toxicity, and bryophytes are unable to fully colonize peatlands within 30 km of the Sudbury smelters (Gignac and Beckett, 1986). Trace metals including Fe, Mn, and Cu ameliorate the toxicity of bisulfate by catalyzing the extracellular oxidation to $SO4^{=}$ (Baxter et al., 1989b). This interaction among pollutants enables *Sphagnum* species to grow in relatively more polluted sites in central England than would be possible in the absence of trace metal pollution. However, the trace metals are not entirely beneficial; Press et al., (1985) demonstrated that concentrations of trace metals in severely polluted English bogs were high enough to inhibit arylsulfatase activity in peat. The catalytic oxidation of SO_2 by trace metals also may be responsible for the ability of *Sphagnum* species to grow in moat areas around the periphery of peatlands located 15 to 20 km from Sudbury smelters; concentrations of Fe and Mn are highest in the moat and decrease toward the center of these peatlands (Gignac and Beckett, 1986). Although many other potential effects of trace metals on peatlands may exist (see discussion below), little research has been performed to document these impacts.

Potential Effects

Acid Deposition

Research of the past 10 years has highlighted many potential effects of acid deposition on peatlands in addition to those effects that have been clearly documented. The magnitude of impacts depends on the intensity, aerial extent, and duration of acid deposition. In many peatlands, the effects will likely be irreversible. Because ecosystems are not wholly self-contained but have numerous biotic, hydrologic, and chemical links with other ecosystems, effects on peatlands may result in serious indirect effects on other ecosystems as well. Although these remain conjectural, it is important to consider such indirect effects in order to fully assess the risks and costs of air pollution.

The results of acid deposition are most easily understood mechanistically by examining the effects of the components of acid deposition: nitrogen, sulfur, and hydrogen ions. In small quantities, addition of N as NO_3^- to peatlands will fertilize the vegetation (Verhoeven et al., 1988; Urban et al., 1989b). Because many peatlands in North America are nitrogen-limited (Watt and Heinselman, 1965; Tilton, 1978), increasing N inputs not only may enhance the growth of existing species, but may allow invasion by other species currently excluded by low N availability (Verhoeven et al., 1983, 1988). In higher doses, NO_3^- will inhibit the growth of some plant species (Woodin et al., 1985; Press et al., 1986; Rudolph and Voight, 1986; Woodin and Lee, 1987). When the capacity of the plants for NO_3^- uptake is exceeded, increased fractions of NO_3^- inputs will be emitted as N_2O or N_2 as a result of denitrification (Hemond, 1983; Koerselman et al., 1989; Urban et al., 1989b). Increased emissions of N_2O must be viewed as undesirable because of their contribution to global warming and stratospheric ozone depletion. High rates of NO_3^- deposition are toxic to bog vegetation (Ferguson et al., 1984; Rudolph and Voight, 1986; Lee et al., 1987).

Effects of increasing S deposition range from changes in S cycling to plant toxicity and loss of plant species. Low rates of S addition are likely to enhance rates of dissimilatory reduction (Behr, 1985; Urban et al., 1989c) resulting in increased emissions of reduced S gases that become reoxidized in the atmosphere and extend the geographic and temporal extent of acid deposition (Nriagu et al., 1987). The increased rate of sulfate reduction also leads to enhanced accumulation of labile, reduced organic sulfur that is readily reoxidized in dry months; such reoxidation leads to flushes of acidic water (Braekke, 1981) or to severe episodes of cation leaching from peatlands (Bayley et al., 1986; Sheppard and Thibault, 1988). Higher rates of S deposition are toxic to bryophytes and lichens (Ferguson and Lee, 1980; Winner and Atkinson, 1987; Looney and James, 1988) and will cause the loss of *Sphagnum* and lichen species (Tallus, 1964; Ferguson et al., 1978; Looney and James, 1988).

The effects of hydrogen ion deposition depend on the extent to which uptake of S and N neutralize the acidity. Because uptake of S and N is neither instantaneous nor 100% efficient (Hemond, 1980; Urban and Bayley, 1986; Urban et al., 1987b, 1989b; Urban and Eisenreich, 1988), much of the H^+ input from acid deposition is not neutralized and may cause cation leaching, site acidification, plant toxicity and species changes, trace metal mobilization and toxicity, decreased decomposition rates, decreased emissions of CO_2 and CH_4, changes in carbon storage rates, changes in production and export of organic acids, and a host of changes in lakes and streams receiving peatland runoff. Enhanced leaching of cations and decreased base saturation of peat as a result of acid deposition have been documented (Urban and Bayley, 1986; Skiba et al., 1989). In fens with only moderate base saturation, loss of nutrient cations is likely to result in a sequence of events culminating in a large decrease in pH; major changes in plant species composition, nutrient cycling and retention, rates of gas emissions; and ultimately, changes in hydrology and water quality that will seriously impact streams and lakes (Gorham et al., 1984, 1987). The pH of fens is determined by the balance between bicarbonate inputs from ground or surface waters and the production of organic acids. The pH will remain above 5.5 as long as the supply of bicarbonate exceeds production of organic acids, but will fall rapidly to about 4 as organic acids predominate over bicarbonate (Urban and Eisenreich, 1989). Acid deposition may induce this large, rapid pH change both by directly titrating inputs of bicarbonate and by leaching cations from surface peat. The reduced base saturation of the surface peat will favor rapid colonization by acidophilic *Sphagnum* species (Clymo and Hayward, 1982; Clymo, 1987; Gorham et al., 1987) that further acidify the site by decreasing decomposition rates (Verhoeven et al., 1990), and thereby promoting accumulation of organic matter that isolates the vegetation from base inputs in groundwater (Bellamy and Riely, 1967; Glime et al., 1982; Wilcox et al., 1986). Eventually this buildup of organic matter is likely to result in decreased water flow through the site and increased concentrations of organic acids. The reduced groundwater inputs and increased organic acid concentrations cause further cation leaching as well as mobilization of trace metals and phosphorus (Richardson, 1985; Wieder and Lang, 1986; Verhoeven et al., 1988). The effects of acid deposition on poor fens is thus likely to greatly accelerate their natural conversion to acidic bogs.

The effects of such acidification are not confined within peatlands. The rapid change in plant and microbial species may result in the complete disappearance of species unique to poor fens (Gorham et al., 1984). The long-term implications of such biotic impoverishment are not fully understood, but may represent a loss of potentially valuable resources, and may preclude the reversibility of the environmental changes (Gignac and Beckett, 1986; Gorham, 1988b). Bird, insect, amphibian, and mammal species would be affected by habitat acidification (Karns, 1984). Fish, invertebrates, and algae in streams and lakes would be impacted by increased concentrations of organic acids and trace metals as well as altered water retention.

Trace Metals

Potential results of atmospheric deposition of trace metals to peatlands include loss of sensitive species, declines in rates of primary production and decomposition, facilitation of the methylation of select metals and uptake by biota, and mobilization of metals into streams and lakes. The deleterious effects of high rates of trace metal deposition in the vicinity of metal mining and smelting have been documented for peatlands, lakes, forests, and grasslands (Gorham and Gordon, 1963; Gignac and Beckett, 1986). Two unique attributes of peatlands render them both more susceptible to harm from trace metal deposition and prone to facilitate the transfer of trace metals into food chains and adjacent streams and lakes.

The first attribute is the high organic matter content and ion-exchange capacity of surface plants (mosses and lichens) and soils. Thus, peatlands have a large capacity to retain and concentrate cationic metals. Trace metals sequestered from atmospheric deposition or surface waters can build up to very high concentrations in peat; concentrations up to several percent have been reported for Cu, Pd, and Fe (Fraser, 1961; Coker and DiLabio, 1979; Crerar et al., 1979). This increases the likelihood of toxicity to both plants and herbivorous animals.

The second attribute is the high concentration of organic acids in peatland waters that act to mobilize trace metals into the water. This phenomenon is most pronounced in acidic bogs where concentrations of dissolved organic matter are much higher than in less acidic peatlands. The results of this mobilization are to render metals more bioavailable, enhance the toxicity to plants, and promote the leaching of trace metals from peatlands into streams and lakes. Although the metals that are mobilized are largely complexed by dissolved organic matter, they remain available and toxic to plants. Organically bound Al has been shown to be taken up to a greater extent than free Al^{+3} and to elicit similar toxic effects in tree seedlings (Arp and Ouimet, 1986; Hutchinson et al., 1986). Sparling (1967) hypothesized that Al concentrations in peatland waters in the British Isles regulated the distribution of the rush, *Schoenus nigricans*. Significant leaching of Pb, Cd, Al, Fe, and Hg from peatlands into lakes and streams occurs because of high concentrations of dissolved organic matter in peatland runoff (Lodenius et al., 1983, 1987; Turner et al., 1985; Urban et al., 1987b; Helmer et al., 1990). The organic acids from bogs may inhibit demethylation of Hg in lakes and thus promote the bioaccumulation of this toxic metal in acidic, brown-water lakes (Xun et al., 1987). Again, linkages among peatlands and other ecosystems may be disrupted or may transfer the ecological damage of air pollutants from peatlands to other sites.

Synthetic Organic Chemicals

Potential effects of atmospheric deposition of synthetic organic chemicals in peatlands include inhibition of microbial activity, inhibition of plant growth, declines or loss of populations of sensitive plant and animal species, and incorporation of toxins into food chains resulting in stress to individuals and populations at the top of the food chain. Although definitive proof of such effects is lacking because of the dearth of research in this area, preliminary evidence gives reason for concern. The vast wetlands in the Hudson and James Bay lowlands are a major breeding ground for numerous species of waterfowl. High concentrations of industrial and agricultural chemicals have been measured in the peatlands and rivers of this remote region (McCrea and Wickware, 1986; McCrea and Fischer, 1986). These chemicals can only have reached these sites through atmospheric transport and deposition. Deposition is facilitated by the cold temperatures that lead to condensation of the chemicals onto atmospheric particulates that are subsequently scavenged efficiently by precipitation (Gregor and Gummer, 1989). High concentrations of organic contaminants in precipitation and wildlife in the Arctic (Muir et al., 1988; Norstrom et al., 1988) attest to the potential for harm throughout latitudes north of 50°.

The potential for ecological damage from agrochemicals also is significant in more southerly regions of intense agricultural activity. Microcosm studies have shown that concentrations of herbicides in runoff reaching midwestern wetlands are adequate to cause acute toxicity to invertebrate populations (Huckins et al., 1986). Nitrification is known to be inhibited in fens and soils receiving aerial drift of herbicides (Rajagopal and Rao, 1984). Significant aerial drift of agrochemicals into a nontidal estuary also has been measured; its effects remain under investigation (Howe, 1990). The persistence of many of these compounds in peatland environments (Rapaport and Eisenreich, 1988) not only increases the potential for chronic, long-term effects, but also may prolong the environmental recycling of these compounds for many years to come (Eisenreich, 1987).

Radionuclides

The ability of mosses and lichens to accumulate and concentrate radionuclides is well documented (Gorham, 1958a, 1959; Persson, 1970; Daroczy et al., 1988; Henderson, 1988). Thus, the potential exists for direct mutational effects to these species as well as for organisms consuming these plants. The Laplanders and their reindeer are probably the most publicized populations at risk (Persson, 1970).

CONCLUSIONS

There is ample documentation of damage caused to peatlands by atmospheric pollutants. There is an abundance of data suggesting that many other effects may exist, but little research has been performed to document the impacts of many pollutants. Air pollutants are likely to induce not only direct effects on peatlands, but also are likely to disrupt the important linkages between peatlands and adjacent ecosystems. The ramifications of many changes caused by pollutants are not understood at present and may not be evident for some time. The probability and potential for serious consequences of the existing widespread exposure of ecosystems to low levels of multiple contaminants demands greater research and regulatory attention.

USE OF THE PHYTOTOX DATABASE TO ESTIMATE THE INFLUENCE OF HERBICIDE DRIFT ON NATURAL HABITATS IN AGROECOSYSTEMS

James E. Nellessen and John S. Fletcher

Dept. of Botany and Microbiology
University of Oklahoma
Norman, OK

INTRODUCTION

In agroecosystems, there exists a patchwork of row crops intermixed with pasture and natural plant communities. The extensive use of herbicides in various agroecosystems across the United States poses a potential threat to vegetation growing on adjacent land if the chemicals applied to cropland inadvertently drift onto nontarget areas. Adverse consequences of such an event could be: (1) reduced production of plant biomass (yield), and/or (2) change in the species composition of the nontarget plant community. Whether or not a plant community is affected in either or both of these ways is dependent on two factors: (1) the nature of the exposure and (2) the sensitivities of the plant species within the nontarget community.

Estimating chemical exposure of nontarget plants depends on several variables: (1) the chemical gradient (concentration vs. distance) extending across the nontarget zone, (2) duration of exposure, and (3) frequency of exposure. The magnitude of each of these variables depends in turn on the chemical and physical properties of the compound, mode of application, and prevailing weather conditions. Because all of these parameters can be quantified, the process of predicting the amount of drift and subsequent exposure of nontarget vegetation lends itself to mathematical modeling. A variety of distinctive models have been developed by various investigators to deal with different combinations of pesticide application (plane vs. tractor), chemical features (liquid vs. dust), and mode of drift (direct from applicator, or indirect following volatilization from field).

The response of nontarget vegetation to pesticide drift has received less attention than development of the drift models. Some models appear to have never been validated by biomonitoring (Thompson, 1983), and others have only been validated by examining cultivated crops (Yates et al., 1978). There are only a few isolated reports on how herbicides influenced the productivity or composition of native plant communities (Malone, 1972; Marrs, 1985; Gillen et al., 1987; Marrs et al., 1989; Swindell et al., 1989). Only one of the reports was conducted in connection with drift modeling, one dealt with a tree community, and none considered the influence of indirect (field volatilization) drift.

In the absence of such studies, an alternative is to use dose-response data taken from the literature for individual plant species that are known to be present in natural plant communities frequently found in pesticide treated agroecosystems. The dose-response data compiled in the PHYTOTOX database (Royce et al., 1984) is ideally suited for predicting potential hazards posed by pesticide drift to nontarget vegetation. In this pilot study we used a portion of PHYTOTOX to predict the potential hazard posed by the volatilization and drift of trifluralin and alachlor on forest communities in Illinois.

MATERIALS AND METHODS

The PHYTOTOX database is a computerized information resource that permits the rapid retrieval and comparison of data pertaining to the response of terrestrial plants to the application of organic chemicals (Royce et al., 1984). As of January 1, 1990, PHYTOTOX possessed information on approximately 8,000 different chemicals, 2,000 species, and 50 plant responses. The data has been compiled from over 3,500 articles published between 1926 to 1988. The database has two files: a Bibliographic file and an Effects file. The Bibliographic file possesses information on each paper that has been used as a source of data for compiling effects records. The Effects file contains approximately 100,000 records. The Effects file differs from most biological databases, because it contains quantitative numerical data pertaining to chemical doses, plant responses, and experimental parameters. Each record in the Effects file contains information concerning the effect(s) of one dose of a single chemical applied to a particular plant species as reported in one publication. The information associated with each record is organized under labels that may be sorted separately during computer searches.

Trifluralin and alachlor were examined in this study, because of their high usage on corn and soybeans in Illinois (Gianessi and Puffen, 1988)), and their strong tendency to volatilize from the soil (Glotfelty et al., 1984, 1989). Attention was focused on the oak-hickory community because small wood lots meeting this description are interdispersed among corn and soybean fields in Illinois (Kuchler, 1964). A hierarchal search of PHYTOTOX was conducted to recover data pertaining to oak-hickory community plants treated with comparative doses (kg/ha) of either trifluralin or alachlor.

RESULTS

PHYTOTOX possessed information on 100 species which occur in oak-hickory communities. This number was reduced to eight when only records pertaining to trifluralin and alachlor were considered (Table 1). The plant list was expanded to include data on an additional 10 species that are in the same genera as plants found in oak-hickory communities. Justification for expanding the list in this manner comes from previous analyses where it was shown that species within the same genus had a high correlation of response to the same chemical (Fletcher et al., 1990).

Examination of the data in Table 1 shows that different species vary widely in their sensitivities, and a single species will respond differently to different herbicides. For example, while *Senecio vulgaris* experienced 100% control (kill) when treated with 1.9 kg/ha alachlor, it was not affected at all by a somewhat lower dose of trifluralin. This variable response by different plant species to chemicals has been capitalized on in selectively killing unwanted plants in cultivated fields. This feature also has the potential of reducing plant biodiversity in nontarget areas if the amounts of drifting chemicals reach the inhibitory level for sensitive plants.

Trifluralin is an extremely volatile herbicide. It has been shown that 90% of the trifluralin applied to moist soil will be lost to the air in 2 to 7 days following application (Glotfelty et al., 1984). These investigators established the maximum rate of volatilization to be 195 g/ha/h and measured air concentrations as high as 40 $\mu g/m^3$ (0.003 ppm) at 50 cm above the soil surface. Based on these data it can be hypothesized that if 2.8 kg/ha is applied to a cultivated field it is possible that moving an air mass could transport 2.5 kg/ha to adjacent nontarget plants over a 2 to 7 day period. When this level of exposure is compared to dose-response data in Table 1, it was found that eight different genera (*Acer, Cassia, Dioscorea, Ilex, Rhododendron, Solanum, Thuja,* and *Urtica*) had sensitivities low enough to be affected. Among these genera the species *Urtica chamaedryoides* is on the Illinois endangered and threatened species list.

TABLE 1. DOSE-RESPONSE DATA FROM PHYTOTOX FOR TWO HERBICIDES COMMONLY USED IN ILLINOIS AND TAXA FROM GENERA KNOWN TO OCCUR IN ILLINOIS WOODLOTS.

	Herbicide			
	Trifluralin		Alachlor	
Plant Species	Dose (kg/ha)	Response[a] (%)	Dose (kg/ha)	Response[a] (%)
Acer palmatum[b]	3.1	20 injury	6.2	injury
Cassia obtusifolia[b]	0.9	81 control	1.7	23 control
Dioscores sp.	0.2	3 DMD		
Euonymus fortunei[b]			20.0	49 DMI
Ilex cornuta[b]	8.9	16 RT FMD		
Ilex crenata[b]	2.5	18 LF CHL	12.5	6 SZI
Juniperus horizontalis			13.6	None
Pinus echinata	1.1	None		
Pinus strobus	4.5	None		
Rhododendron obtusum[b]	2.5	35 TRD	6.0	9 injury
Sedum brevifolium[b]			2.5	15 injury
Senecio vulgaris[b]	1.1	None	1.9	100 control
Solanum nigrum	0.6	15 control		
Solanum sp.	0.6	35 control		
Thuja occidentalis	0.6	3 TRD	13.6	None
Urtica urens[b]	2.5	100 kill	1.9	100 control

[a] All responses refer to whole plants unless indicated otherwise. Control = similar in meaning to plant kill, DMD = dry mass decrease, DMI = dry mass increase, LF CHL = leaf chlorosis, RT FMD = root fresh mass decrease, SZI = size increase, TRD = transpiration decrease.

[b] Taxa that do not occur in Illinois woodlots but are members of genera that can be found in Illinois woodlots.

Alachlor has a lower field volatility than trifluralin, but even at the reduced rate of 8.1 g/ha/h it has been shown that 19% of applied doses (420 g/ha) were lost in 21 days (Glotfelty et al., 1989). If weather conditions caused this amount of volatilized alachlor to be redeposited on vegetation adjacent to an applied field it could influence the growth of three genera listed in Table 1. This level of alachlor exposure represents 25% of a dose giving 23% control of *Cassia obtusifolia* and 22% of a dose giving 100% control of *Urtica urens* and *Senecio vulgaris* (Table 1). Two species of *Cassia*, three of *Senecio*, and the aforementioned *U. chamaedryoides* growing in Illinois woodlots could be affected.

CONCLUSIONS

A comparison between maximum drift values estimated from the literature with dose-response data taken from PHYTOTOX indicated that some nontarget species growing in oak-hickory communities could be influenced by the drift of trifluralin and/or alachlor. The most sensitive plants were *Cassia* and *Urtica*. Although we are not aware of any field measurements or biomonitoring data collected in native plant communities which would substantiate this prediction, there is a report by Behrens and Lueschen (1979), where 0.28 kg/ha of dicamba applied to a corn field affected soybean growth 60 m downwind in an adjacent field. Such data certainly is cause for concern and suggests that herbicide drift may have a profound influence on the productivity and composition of natural plant communities.

The biota of the United States has been described as having approximately 116 different native plant communities (Kuchler, 1964). The geographical location and species composition of each of these communities is known. Therefore, it is possible to identify natural plant communities that are in association with various crops in different agroecosystems located throughout the United States. In this pilot study with PHYTOTOX we considered only one plant community (the oak-hickory forest) and only two herbicides (trifluralin and alachlor). Similar analyses could be conducted for all 116 plant communities in the United States and also for an extended list of herbicides.

BIOLOGICAL MARKERS IN ANIMALS AND PLANTS TO ESTABLISH EXPOSURE TO, AND EFFECTS OF, ATMOSPHERIC TOXICANTS

John F. McCarthy and Timothy J. Tschaplinski

Environmental Sciences Division
Oak Ridge National Laboratory
Oak Ridge, TN

ABSTRACT

Evaluation of the potential for exposure to toxicants transported through the atmosphere is extremely complex due to the diversity of possible routes of exposure, differences in bioavailability, and the complexity of molecular, biochemical, and toxicological interactions within exposed organisms. This complexity limits our capabilities to either quantify or assess the significance of exposure to atmospheric toxicants. Exposure cannot be readily quantified by measuring body burdens of contaminants because many deleterious chemicals are rapidly metabolized. Furthermore, the relationship between body burden and toxic response is complex and not fully understood. Assessing the significance of exposure to complex mixtures of chemicals is even more problematic. Chemical analyses are difficult and expensive; furthermore, possible synergistic or antagonistic interactions within biota can invalidate predictions based on toxicity of individual chemicals.

The overall objective of our research is to develop and validate the concept of using animals and plant biomarkers as indicators of bioavailable contaminants. Evidence of exposure in animals or plants provides a temporally integrated measure of bioavailable contaminant levels, and is therefore much more relevant to the potential risk to health or the environment than is the analytically measurable concentration of contaminants in the soil, water, or air.

Our approach is to measure biomarkers (biochemical or molecular indicators of exposure) in environmental species as sensitive, biologically relevant indicators of toxicant exposure. Biomarkers under study include several measures of either specific damage to DNA (e.g., adducts) or non-specific damage to the integrity of the genetic material (e.g., DNA strand breaks), induction of several detoxification systems (mixed function oxidase system, metallothionein, and oxyradical scavenging enzymes), as well as biomarkers of reproductive competence. The qualitative pattern and quantitive response of a suite of biomarkers offers the potential of indicating the extent of exposure to atmospheric pollutants, and the magnitude of the toxic effects from that exposure. Challenges that

must be resolved before applying this approach to regional studies include establishing an acceptable reference level of biomarker response in "unexposed" animals or plants, and understanding the effect of environmental and physiological variables on biomarker responses of individual organisms.

INTRODUCTION

The U.S. Environmental Protection Agency is mandated to protect human health and the ecological integrity of the environment from unreasonable risks associated with exposure to pollutants. Although existing regulations are targeted at a wide range of possible sources of contaminant input to the environment, there is an increasing concern about the effects of the plethora of anthropogenic chemicals capable of being transported long distances through the atmosphere. These chemicals include trace metals, industrial organic compounds, including polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), as well as chlorinated pesticides, and gaseous toxicants; such as SO_2, NO_x, and O_3. The effects of chronic deposition of airborne toxic chemicals on the integrity of terrestrial and aquatic ecosystems is not known, especially with respect to the potential interactions of these toxicants with other environmental or physiological stresses.

This paper will discuss an approach that can contribute to evaluating the exposure of organisms to airborne toxicants, and can be particularly valuable as a tool to evaluate the biological significance of that exposure (NRC, 1987). The approach is based on biological monitoring of animals and plants in areas impacted by airborne toxicants, and, more specifically, on measurements of molecular, biochemical, and physiological biological markers (biomarkers) in target species. In this context, the measurements of body burdens of persistent compounds (or metabolites) and of biomarkers of exposure or effects permit the animals and plants to serve as biomarkers indicating the presence of bioavailable contaminants.

Biological monitoring has a number of advantages that make it an informative and necessary adjunct to measurements of the concentrations of chemicals in the environment. Chemical measurements of environmental media are specific, quantitative, and exquisitely sensitive and precise. However, the biological significance of the chemical concentrations measured in air, water, soil, or food is not at all clear. We understand the toxic action of only a few of the thousands of chemicals in the environment and have almost no information on the toxicity of complex mixtures of chemicals or on the role of environmental stresses on an organism's susceptibility to toxic exposure. Furthermore, a chemical survey is a snapshot in time and space. Variations in concentrations over time resulting from intermittent releases of effluents by industries, or from storm events, changes in winds, and such, cannot be accounted for without repeated analyses. Spatial patchiness of contaminant patterns also requires extensive and expensive sampling and chemical analyses.

One approach to addressing these problems is to monitor animals and plants in the environment as sentinels of environmental contamination. Evidence of exposure in sentinel species provides a temporally integrated measure of bioavailable contaminant levels and is therefore much more relevant to the potential risk to the environment than is the analytically measurable concentration of contaminants in the soil, water, or air. Measurements of body burdens of persistent compounds provides a direct measure of compound uptake. Measurements of biomarkers provide the following information that cannot be obtained from direct measurement of body burdens and that is very relevant to evaluating the potential biological and ecological effects of toxicants:

- Provide evidence of exposure to compounds that do not bioaccumulate, or are rapidly metabolized and eliminated.
- Integrate the toxicological and pharmacokinetic interactions resulting from exposure to complex mixtures of contaminants, and present a biologically relevant measure of toxicant interactions at target tissues and the cumulative adverse effect of the exposure.
- Give quantitative measures of adverse effects in sentinel species, and are therefore relevant to understanding the relationship between exposure to environmental levels of airborne contaminants, and the potential for adverse health and ecological effects of air toxicants.

This paper will describe several biomarkers of exposure and effect as they have been applied to assessing exposure of animal populations. We will then describe the use and potential application of several biomarkers of airborne toxicants in plants. Finally, the advantages and difficulties in applying this approach to assessing the effects of airborne toxicants will be evaluated.

BIOMARKERS OF EXPOSURE AND EFFECTS IN ANIMALS

Selection of specific biomarkers will depend on the physical and chemical properties of the toxic chemical, the depth of current understanding of its mode of toxic action, the metabolic capabilities of the sentinel species, and the objective of the monitoring effort (e.g., is the emphasis on assessment of exposure or effects). In all cases, the response of animals from areas of suspected contamination must be compared to those of organisms from ecologically comparable reference sites that are known to be free of anthropogenic toxicants. Only a minimal number of animals are sacrificed to carry out the chemical analysis. The concept of biomarkers is illustrated in Figure 1. Several classes of biomarkers have been used for environmental monitoring and offer promise as sensitive measures of exposure and informative measures of effect.

Biomarkers of Exposure

Biomarkers of exposure are indicators of an exogenous substance within an organism (including body burden of parent compound or metabolites), interactive products formed between the chemical and endogenous components, or an event in the biological system that can be directly related to exposure (NRC, 1987). Several categories of biomarkers of exposure are described generically in the following discussion.

Biomarkers of Genetic Damage

These can include both measures of damage from specific chemical agents or can be nonspecific indicators of damage to the integrity of the DNA. The latter biomarkers are especially useful because they are a measure not only of agents that can directly damage DNA, but they can also assay the activity and fidelity of the mechanisms responsible for proof-reading and repairing DNA:

(1) DNA adducts - The metabolism of chemicals may result in the production of highly reactive electrophilic metabolites that can undergo attack by nucleophilic centers in macromolecules such as DNA, RNA, or proteins. The amount of the reaction product (adducts) is proportional to the *in vivo* concentration of the electrophile and length of the exposure. Therefore, the amount of metabolite bound to cellular DNA (*in vivo* dose) provides a reliable dosimetric basis upon which to assess exposure to a genotoxic compound (Table 1; Perera et al., 1982; Shugart et al., 1987; Shugart et al., 1989).

(2) DNA strand breaks - Certain genotoxic compounds or agents such as metals, radionuclides, and some chemicals do not covalently bind to DNA, but nevertheless induce damage. If this damage is expressed as single-strand breaks (or the potential for single-strand breaks), it can be detected by measuring the rate of alkaline-induced strand separation (Rydberg, 1975; Shugart, 1988; Shugart et al., 1989). This technique provides a general measure of DNA damage because sites modified by adducts may also be alkaline labile (Figure 2; Kanter and Schwartz, 1982; Daniel et al., 1985).

(3) Cytogenetic damage - Chemical and physical agents that are genotoxic can produce damage to DNA that propagate into morphologically detectable chromosomal aberrations.

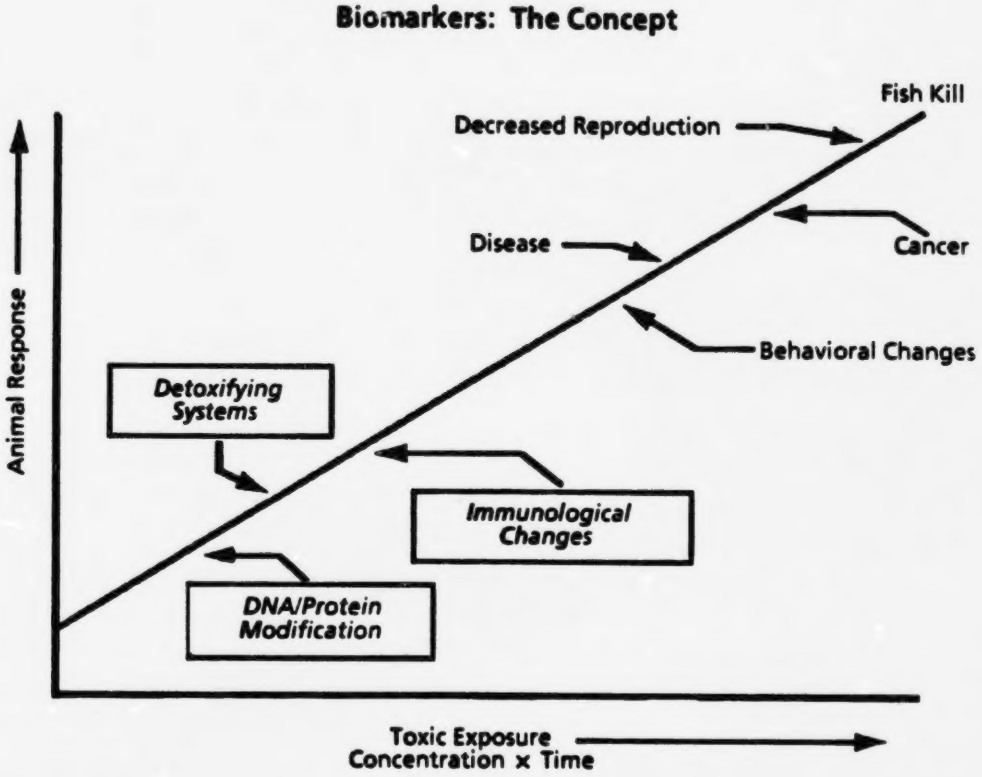
Biomarkers: The Concept
Fish Kill
Decreased Reproduction
Disease
Cancer
Behavioral Changes
Animal Response
Detoxifying Systems
Immunological Changes
DNA/Protein Modification
Toxic Exposure
Concentration x Time

FIGURE 1. **The Biomarker concept.** The response of an animal to toxicant exposure is a function of the concentration of a chemical in the environment and the length of time the animal is exposed. We would like to avoid the long-term, irreversible adverse effects indicated in the upper right hand portion of the figure. The biomarker approach seeks to measure early responses indicated in the boxes at the lower left of the figure. These sensitive biological markers indicate that the animal has been exposed to chemicals in the environment and provide an early warning of future effects.

TABLE 1. Benzo[a]pyrene adduct formation in DNA isolated from brain tissue of beluga whales[a]. The whale population from the St. Lawrence River in Canada is declining and there have been several beached whales with bladder tumors. The area from which the whales were collected is known to have measurable levels of PCBs and PAHs, including benzo[a]pyrene. The data below quantify "adducts" [the amount of a carcinogen, such as benzo[a]pyrene (B[a]P), chemically attached to DNA]. DNA from the affected population of beluga whales from the St. Lawrence River has been modified by B[a]P at levels as high as those observed in mice and fish experimentally exposed to a carcinogenic dose of the chemical; belugas from a pristine area in Canada's Northwest Territories had no detectable adducts (Martineau et al., 1988).

	B[a]P Adduct Formation		
Sample	Tissue	Binding[b]	Level[c]
St. Lawrence Estuary			
#1	Brain	206	2.15
#2	Brain	94	0.98
#3	Brain	69	0.73
MacKenzie Estuary			
#1-4	Brain	None detected	
#1-4	Liver	None detected	

[a] DNA isolation and quantitation was according to Shugart et al. (1983)

[b] B[a]PDE-DNA adducts expressed as nanograms of tetrol I-I (resulting from binding to DNA of the anti-B[a]PDE metabolite of benzo[a]pyrene per gram of DNA (see Shugart et al.,1983).

[c] Level expressed as number of B[a]PDE-DNA adducts per 10^7 DNA nucleotides.

The cytogenetic assays currently in use represent a highly diverse group of tests which include measures of DNA repair processes, mitotic recombination, sister-chromatid exchange, and such. Petrochemical-related DNA damage in wild rodents has been detected by these methods (McBee and Bickham, 1988).

Protein adducts

Hemoglobin has been proposed as an alternative cellular macromolecule to DNA for estimating the *in vivo* dose of chemicals subsequent to exposure (Osterman-Golkar et al., 1976; Calleman, 1984; Shugart and Kao, 1985; Shugart, 1985a, b; Shugart, 1986) because it has reactive nucleophilic sites that form stable reaction products with electrophilic agents; no mutagenic or cancer-initiating compound has failed to produce covalent reaction products with hemoglobin. This approach has been used to monitor exposure in animals from a floodplain in Oak Ridge, TN, contaminated with PAH, and has demonstrated that the concentration of hemoglobin adducts of benzo[a]pyrene were highest in animals with the greatest contact with the contaminated soil (Loar et al., 1987b).

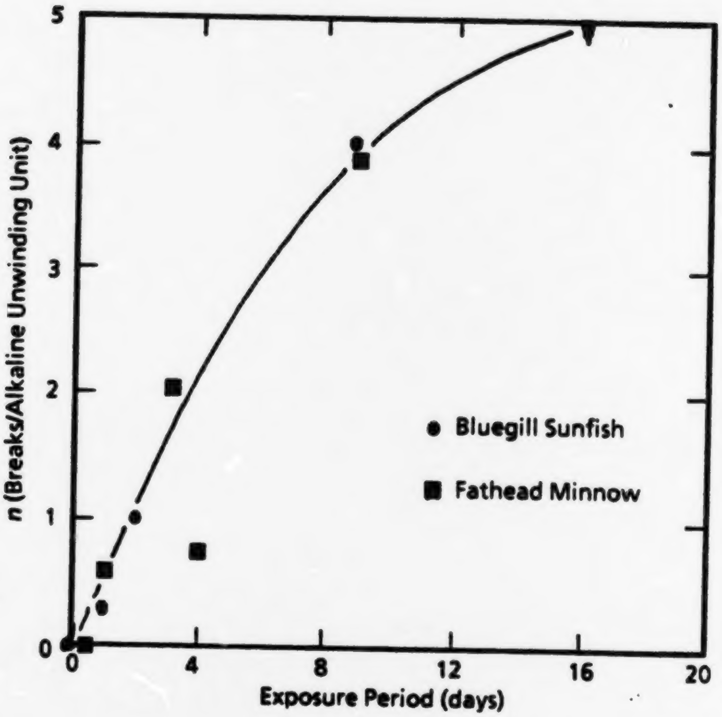

FIGURE 2. Time course of genetic damage, measured as the number of single-strand breaks in DNA through the use of an alkaline unwinding assay, in fish exposed to the carcinogen benzo[a]pyrene (BaP) in the laboratory. Bluegill sunfish and fathead minnows were exposed under flow-through conditions to an aqueous solution of BaP (l ug/L) for 20 d. Results are plotted as the number of breaks per alkaline unwinding unit, in the manner of Rydberg (1975) and Shugart (1988).

Induction of Detoxication Systems as Biomarkers

Most contaminants stimulate synthesis of protective detoxication systems. Higher levels of these proteins are diagnostic of a molecular response to toxicant exposure. Several classes of detoxication systems, each responding to specific classes of toxicants, are available as biomarkers:

(1) Mixed Function Oxidase System - The oxidation of many xenobiotic organic compounds is catalyzed by a group of hepatic cellular monooxygenases. The biochemical system responsible for these oxidation and conjugation reactions are similar in vertebrates ranging from fish to mammals (Bend and James, 1979; Chambers and Yarbrough, 1976). Because chronic exposures to many organic contaminants induce the hepatic MFO system in fish (Leck et al., 1982; Price-Haughey et al., 1986; Jimenez et al., 1987; Jemenez and Burtis, 1989; Loar, 1987a,b) and mammals (Alvares et al., 1967; Sladek and Mannering, 1966; Lu and West, 1980), the levels of components of this system provides evidence of exposure and effects of many compounds that are rapidly biotransformed by the detoxication system (Figure 3; Payne, 1984).

(2) Concentrations of Metal-Binding Proteins (Metallothionein) - Almost all organisms possess low molecular weight proteins capable of binding toxic metals such as cadmium, zinc, or copper, and rendering them unavailable for toxic actions within cells. The levels of these proteins, including the cysteine-rich metallothionein, are induced in many organisms chronically exposed to toxic metals in the environment (Kojima and Kagi, 1978; Webb, 1979; Mitane et al., 1986; Hamilton and Mehrle, 1986; Harrison et al., 1987). Quantification of metal-binding proteins is a promising biomarker for exposure to a range of heavy metal contaminants, such as cadmium and zinc (Table 2).

(3) Oxyradical Generation and Oxidative Stress - A large number of diverse organic compounds can undergo redox cycling (Mason and Chignell, 1982; Kappus, 1987) in which the parent compound first undergoes a one-electron reduction to form an organic radical, with the electron subsequently donated to molecular oxygen, giving rise to $O_2^{\cdot}$. Superoxide may have deleterious effects, or may give rise to other toxic oxyradicals - H_2O_2 and OH - that have been associated with a number of toxic effects, including altered redox status, lipid peroxiolation, protein oxidation, and damage to DNA (Fridovich, 1983; Halliwell and Gutteridge, 1984; Kappus, 1987). Additionally, oxidative stress can invoke adaptive responses, such as inductions of antioxidant enzymes (e.g., superoxide dismutase, catalase, and glutathione peroxidase), which can be used as biomarkers. For example, induction of superoxide dismutase has been demonstrated in fish exposed to a range of organic compounds (Washburn and DiGiulio, 1989; Mather-Mihaich and DiGiulio, 1986).

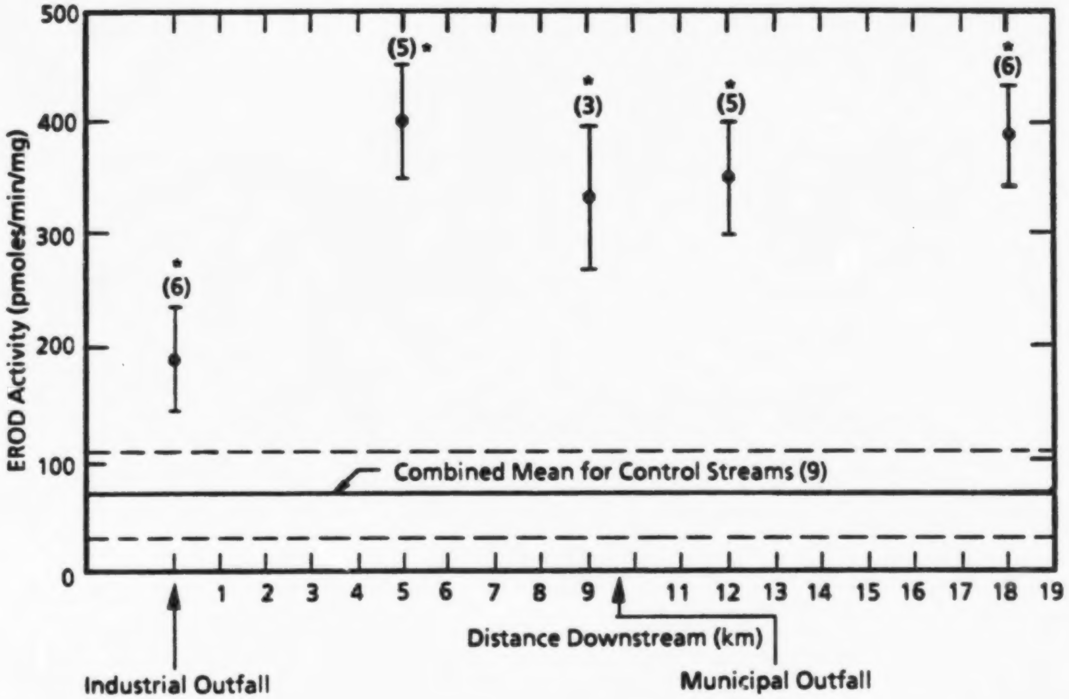

FIGURE 3. Induction of detoxication enzymes in fish. Fish in a stream contaminated by industrial effluents demonstrate significantly higher levels of a detoxication system, the mixed function oxidase system. The levels of one enzyme activity of this system, ethoxyresofurin-)-deethylase (EROD), is measured in depatic microsomes of bluegill sunfish collected in East Fork Poplar Creek (Oak Ridge, Tennessee) at different distances downstream from an industrial source (New Hope Pond) and compared to EROD levels in fish collected at the same time from Brushy Fork Creek, an unpolluted reference stream. Each point represents the mean +/- S.E.M. (n) for each station. Significant differences (P <0.01) between the combined mean (________)+- SEM (----) for the reference stream ("control stream") and for the stations in the stream receiving the industrial effluents are indicated by asterisks (see Jimenez et al., 1988).

TABLE 2. Metal-binding proteins (MBP) in the livers of bluegill sunfish (*Lepomis machrochirus*) exposed to cadmium in the laboratory and in redbreast sunfish collected from streams contaminated with metals, including zinc. Fish were injected intreperitoneally with 2 mg Cd/kg body weight as $CdCl_2$ in 0.9% saline on each of three consecutive days and then sacrificed on Day 6. Control fish were similarly injected with 0.9% saline (50uL/10[illegible] g body weight) on each of three consecutive days and sacrificed on Day 6. White Oak Creek drains the southern boundary of the Oak Ridge National Laboratory and flows into White Oak Lake. Brushy Fork Creek is used as a reference site because it has no inputs of industrial or other point source pollutants. MBP concentrations in livers were measured by the use of the Chelex-100/^{109}Cd procedure (Sloop, personal communication), and are reported as nanomoles of ^{109}Cd bound per gram of soluble protein ± S.E.M.

Sample Description	MBP Concentration
Laboratory Exposure (cadmium)	
Control	247 ± 168 (n = 4)
Exposed	977 ± 133 (n = 3)*
Field Collection	
Reference Stream (Brushy Fork Creek)	631 ± 121 (n = 4)
White Oak Creek (3.03-3.4 km)	1900 ± 306 (n - 10)*
White Oak Creek (2.5 km)	1732 ± 368 (n = 6)*
White Oak Lake	1472 ± 404 (n = 4)*

* MBP concentrations are significantly different from those in control or reference animals at alpha = 0.05.

Biomarkers of Toxins with Specific Modes of Action

Certain compounds exert their toxic action through specific and well understood mechanisms. Measurements of these key toxicological endpoints can be interpreted as biomarkers. For example, neurotoxins such as pesticides act by inhibiting the activity of the enzyme, acetylcholinesterase. Reduction in the activity of this enzyme in plasma or in brain tissue is a biomarker of exposure to this class of toxicants. Similarly, the activity of the enzyme aminolevulinic acid dehydrase, an important component in the porphyrin biosynthetic pathway, is inhibited by heavy metals, and is particularly diagnostic of toxic exposure to lead. Many other examples of potential biomarkers can be selected, depending on the potential toxicants of concern at a particular site.

Biomarkers of Effects

The division between biomarkers of exposure and of effects is somewhat arbitrary. For example, depression of acetylcholinesterase levels is a biomarker of exposure to a specific class of toxicants, but also indicates the magnitude of the neurotoxic effect of the exposure. In the context of this discussion, a measurement of impaired function at some level of biological organization is considered a "biomarker of effect" that may or may not be attributable to the action of chemical toxicants. Attributing the adverse effect to toxicant exposure will generally require that the response toxicants be propagated to successively higher levels so as to form a chain of logical, albeit circumstantial, evidence that the "effect" is causally related to the exposure. Several different biomarkers of effects classes have been examined in animals and found to be reliable for environmental monitoring.

Biomarkers of Impaired Reproductive Competence

Reproductive capacity is the key process linking exposure and effects of toxic materials within an individual to a population-level consequence. Gonads can be examined to determine parameters such as abnormalities in sperm, numbers of oocytes recruited, and abnormalities in oocyte development quantified as numbers of atretic (dying) oocytes. Effects on the reproductive potential of small mammals can be assessed through counts of corpora lutea, embryos, or placental scars. Effects on avian reproduction can be assessed by nesting success surveys. Reproductive condition of males can be assessed by examining testicular size, which is indicative of sexual maturity and reproductive activity. Reproductive condition of females can be assessed on the basis of whether they are mature or immature, lactating or not, in estrus or not, and whether they are pregnant.

Biomarkers of Impaired Organ or Tissue Function

A number of easily measured parameters can indicate in quantitative terms the physiological and bioenergetic status of the animals. Organ indices (e.g., ratios of the weight of liver and gonads to body weight) and condition indices (ratios of length and width parameters in animals that indicate the "plumpness" of the individual), as well as levels of serum and body lipids and triglycerides all provide useful information on the energy stores of the animals and mobilization of those stores for physiological functions. Serum enzyme levels, including transaminases (SGOT, SGPT), lactic dehydrogenase, and sorbitol dehydrase levels indicate cytotoxic damage, which results in release of these enzymes into the blood. Histopathological analyses of tissues, especially liver, provide evidence of neoplastic, necrotic, or parasitic lesions. These data are not only biomarkers of the effects, but also can aid in interpretation of biomarkers of exposure. For example, contaminant-induced changes in liver enzyme activities can be seriously impaired by the hepatotoxic damage resulting from parasitic or necrotic lesions (McCarthy et al., 1989). Information on serum enzymes or histological evidence of liver damage can help in interpreting the significance of indicators of exposure.

Indicators of General Health Status and Population Age Structure

In addition to information from biomarkers that indicate both exposure and the effects of exposure, a significant body of information can be gathered from observations on the health and age of animals trapped for the population and community studies. For example, gross anatomical examination can identify lesions, tumors, necrosis, liver size, and reproductive condition, and will help determine whether tissues should be subjected to histopathological examination to confirm the presence of tumors or neoplasia. The age structure of the animal populations from different sites can be assessed by a number of observations. Growth rings in fish scales are an accurate indicator of age. In mammals, cranial measurements (degree of fusion of cranial sutures, tooth eruption in young animals, and amount of tooth wear in older animals) provide an indication of relative and absolute age. The weight of the eye lens increases with age. The length of the animal (length from snout to dorsal tip of tail, and length of foot from outside of heel to tip of toes), as well as the overall size of the animal also can be related to age (less mature animals are smaller). The pelage (coat color and condition) is another indication of health. These analyses should provide evidence of premature mortality in populations exposed to contaminants.

BIOMARKERS OF EXPOSURE AND EFFECTS IN PLANTS

The general conceptual approach described for applying biomarker-based monitoring to evaluate the effects of toxic chemicals in animals can be readily adapted to plants (Figure 4). Biomarkers can be defined at different levels of resolution from molecular, cellular, organismal, species, through ecosystem level responses. As with animal systems, there is particular interest in biochemical indicators that may have predictive value in that they precede visual, advanced damage, including mortality, leaf abscission, visible foliar lesions, factors associated with secondary stresses, growth decline, and breakdown of cell ultrastructure (Figure 4). A potential biomarker in plant systems should meet several criteria including (1) rapid and unambiguous response to low levels of toxicants, (2) specific responses for a particular toxicant, (3) simplicity of the measurement, and (4) reproducible results (Arndt, 1970; Darrall and Jager, 1984). A major limitation in plant biomarkers is the lack of specificity in biomarker responses, because several stresses that differ greatly in nature may elicit similar responses.

A suite of markers may, however, prove useful in pinpointing the nature and impact of stress at an affected site. For example, biomarkers that may prove useful as indicators of exposure include metabolite pool size and turnover, detoxifying systems, and DNA/protein modification (Figure 4). The numerous photosynthetic processes, with the exception of pigment concentrations (considered under the metabolite section), may be useful as biomarkers of general effects, but these processes are

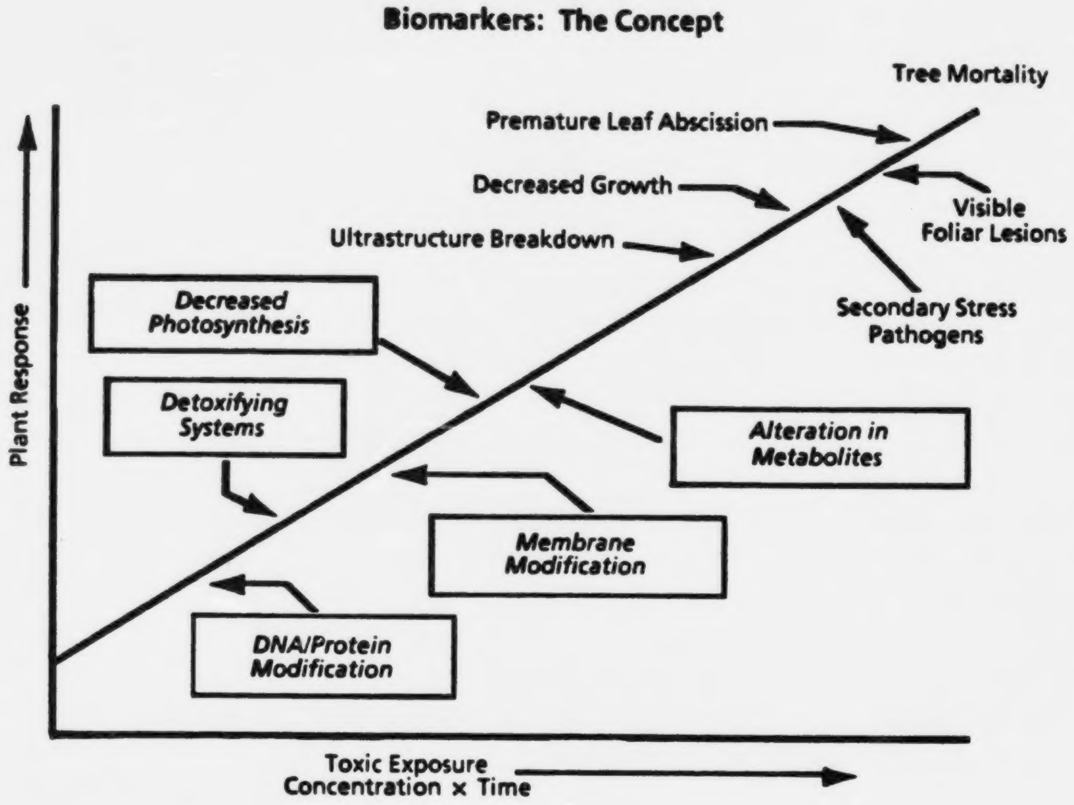
Biomarkers: The Concept
Tree Mortality
Premature Leaf Abscission
Decreased Growth
Visible Foliar Lesions
Ultrastructure Breakdown
Secondary Stress Pathogens
Decreased Photosynthesis
Detoxifying Systems
Alteration in Metabolites
Membrane Modification
DNA/Protein Modification
Plant Response
Toxic Exposure Concentration × Time

FIGURE 4. The biomarker concept as it pertains to plants. The concept is analogous to that described in Figure 1, but reflects key responses of plants to toxicant exposure.

affected by such a variety of environmental and physiological factors that they may be of only marginal utility as indicators of effects that can be associated with pollutants. Photosynthetic processes that could be considered include changes in electron transport, photophosphorylation, fluorescence characteristics, carbon assimilation, partitioning, and allocation. The same lack of specificity also limits the use of membrane modifications as biomarkers, including ion transport, oxidative electron transport, and breakdown of compartmentation itself.

Most data collected on biomarkers of stress relate to heavy metals and gaseous pollutants, including O_3, NO_x, SO_2, HF, and peroxyacyl nitrate (PAN). Because there is a better understanding of plant responses to toxic gases, this discussion will largely focus on the biomarkers of gaseous pollutants, particularly those that are often used, or that appear to offer the greatest potential as indicators of exposure and effects in plants. It must be noted, however, that environmental factors such as temperature, nutrient, and water stress can confound the interpretation of biomarkers. Several detailed reviews report a broad array of biochemical variables that have been correlated with stress (e.g., Koziol and Whatley, 1984; Malhotra and Khan, 1984).

DNA/Protein Modification

Numerous enzymes are impacted directly by environmental toxicants. The primary effect can be a decrease in enzyme activity, but in time protein degradation and synthesis are also impacted by altered DNA transcription.

(1) Ribulose-1,5-Bisphosphate Carboxylase/Oxygenase (RUBISCO) - The activity of the main carboxylating enzyme in C_3 plants, (RUBISCO), has often been targeted as a biomarker. The inhibition of the rate of net photosynthesis (Pn) by SO_2 has been attributed to reduced activity of RUBISCO in *Spinacia oleracea* l. chloroplasts, due to the competitive binding of SO_2 and CO_2 binding sites (Zeigler, 1972). RUBISCO activity also declines with O_3 stress in *Oryza sativa* L. (Nakamura and Saka, 1978). The use of RUBISCO as a biomarker is limited because its activity can be readily altered by growing conditions and nutrient regimes.

(2) L-Phenylalanine Ammonia Lyase (PAL) - PAL activity increases with exposure to O_3 (Tingey et al., 1976a). Several gaseous toxicants, such as O_3, NO_x, and SO_2, stimulate free radical formation (Malhotra and Khan, 1984, Richardson et al., 1989). L-Phenylalanine Ammonia Lyase may increase in response to any oxidizing toxicant as a consequence of tissue disruption that stimulates secondary metabolism, including synthesis of phenolic compounds required in cell wall repair. L-Phenylalanine Ammonia Lyase, and phenolic metabolites may therefore serve as broad-based indicators of oxidant stress, including other stresses that generate free radicals, such as ionizing UV-B radiation.

(3) Glutathione reductase - Given that glutathione is a free radical scavenger, glutathione reductase activity may increase in response to oxidant stress (Bennett et al., 1984) and hence be a useful indicator.

(4) "Metallothionein-like" Complexes - Although a number of gaseous stresses may induce similar responses, recent reports on heavy metal toxicants suggests the production and accumulation of "metallothionein-like" peptide-metal complexes that may be specific for a particular toxicant (Robinson and Jackson, 1986). Such complexes are found in animal systems, as discussed above. Homologous complexes remain to be fully characterized in angiosperms. Robinson and Jackson (1986) isolated a small Cd complex from Cd-resistant *Datura innoxia* Mill. cells containing glutamate, cysteine, and glycine in a ratio between 2:2:1 and 3:3:1, which resembles metallothionein. These peptides are collectively known as poly(-glutamylcysteinyl)glycine (EC)nG. It has been hypothesized that these proteins are involved in metal ion homeostasis, protection from ionizing radiation, and detoxification of free radicals (Karin, 1985; Robinson and Jackson, 1986).

Induction of Detoxifying Systems

Toxicants such as NO_x and SO_2 can be initially detoxified by normal metabolic pathways by increased activity of enzymes involved in assimilation.

(1) Increased Assimilation (e.g., Nitrate Reductase) - Low concentrations of NO and NO_2 are readily converted into NO_3^- and NO_2^- upon dissolution in aqueous solutions, and assimilated by nitrate reductase and nitrite reductase, and then incorporated into nitrogen metabolism in higher plants via glutamine synthetase and glutamate synthase. Given that nitrate reductase activity (NRA) is substrate-inducible, this suggests the possible use of NRA as a biomarker of NO_x impact at nitrogen-poor sites. This has been suggested by Norby (1989), working with high-altitude red spruce (*Picea rubens*). At highly fertile sites the level of constitutive NRA would already be too high to distinguish NO_x impact, and there may be considerable diurnal and seasonal variation in NRA, limiting its use as a biomarker. If plant tissues are exposed to acute levels of NO_x the plant's capacity to metabolize these toxicants via normal metabolic pathways is exceeded and membrane damage occurs due to free radical generation and membrane oxidation.

(2) Free Radical Scavengers - Plants rely on free radical scavenger systems to prevent extensive membrane disruption, similar to animal systems described above. Enzymes in plants that function in scavenging of free radicals and their products include superoxide dismutase, peroxidase (Castillo et al., 1987; Richardson et al., 1989), and catalase (Richardson

et al., 1989). The lack of specificity of the induction of these systems limits their use as specific biomarkers, but they are useful as general indicators of oxidant stress. Nonenzymatic scavengers, including α-tocopherol (vitamin E), ascorbic acid, β-carotenes, and glutathione (Richardson et al., 1989) may also have the same limitation. Metabolites that are indicative of tissue disruption or repair processes may prove more useful.

Specific Metabolites as Biomarkers

(1) Malonaldehyde - A number of studies demonstrate a decrease in lipid content following SO_2, O_3, and NO_2, often due to inhibited synthesis (Mudd et al., 1971a, b; Malhotra and Khan, 1978, 1984). A common finding is the accumulation of malonaldehyde, a product of free-radical peroxidation of unsaturated fatty acids (Mudd et al., 1971b; Khan and Malhotra, 1977; Richardson et al., 1989). Although malonaldehyde concentrations may be a useful general indicator of oxidants that generate free-radicals, it lacks specificity.

(2) Carotenoids - Pigments have recently received attention as possible biomarkers. Photosynthetic pigment concentrations are often reported to decline following exposure to toxicants; however, pigment concentrations may also decline in response to mineral nutrition status, light, temperature, and water stress (Darrall and Jager, 1984). Mehlhorn et al. (1988) have reported that the ratio of violaxanthin/antheraxanthin (two carotenoids) in two-year-old needles, the ratio of dry weight/fresh weight differences between current and two-year-old needles, and ethylene emissions in two-year-old needles were independent of site effects and correlated with Norway spruce (*Picea abies* L) damage in areas affected by forest decline. A strong correlation between ethylene production, and violaxanthin/antheraxanthin ratio was reported by Wolfenden et al. (1988), suggesting the carotenoid ratio, a specific indicator, correlated with the more general stress indicator. The application of the carotenoid ratio test to controlled exposures of various toxicants in other species is required to determine the specificity of this test.

(3) Ethylene Emissions - Ethylene production increased in response to SO_2 exposure (Bressan et al., 1979), and ozone exposure (Tingey et al., 1976b). The use of volatile emissions, such as ethylene, as biomarkers of exposure to toxicants is limited by a lack of specificity; however, ethylene production is recognized as a good general indicator of stress (Abeles, 1973; Kimmerer and Kozlowski, 1982).

(4) Phenol Metabolism - Another general class of compounds that are receiving attention as potential biomarkers are phenols and related metabolites. It is not surprising that concentrations of phenolic compounds increase with oxidant stress, given that the activity of

PAL and polyphenol oxidase (PPO) also increase (Tingey et al., 1976a). Oxidation of phenols by PPO, laccase, and phenolases is involved in the production of polyphenols, flavinoids, and alkaloids (Goodwin and Mercer, 1983). Keen and Taylor (1975) reported that ozone induced large accumulations of isoflavonoids in soybean (*Glycine max* (L) Merr, including daidzein, coumestrol, and sojagol. Hurwitz et al., (1979) reported the accumulation of 4',7-dihydroxyflavone in ozone-stressed alfalfa (*Medicago sativa* L). Tingey et al. (1976b) subjected Ponderosa pine (*Pinue ponderosa* Laws.) to chronic ozone exposures and found that levels of soluble sugars, starch and phenols tended to increase in the shoots and decline in the roots in response to ozone. These studies suggest that there are likely to be several phenols and related metabolites that can be used as indicators of ozone stress.

APPLICATION OF BIOMARKER-BASED MONITORING TO EVALUATE AIRBORNE TOXICANTS

The concept of using biomarker measurements in animals and plants for assessing exposure and effects due to toxic chemicals in the environment has generally been limited to localized "hot spots" of contamination, such as polluted streams, rivers, or harbors. In general, results have been encouraging; biomarker responses have correlated with the perceived degree of contamination, and the relative ranking of sites on the basis of molecular and biochemical responses agrees well with community level measures of ecosystem integrity (Loar, 1987a, b). In these applications, as in applications for evaluating airborne toxicants, the biomarker approach offers valuable information that links exposure to effects and that offers the potential of predicting the potential for long-term ecological effects from rapidly responding biomarkers. However, airborne toxicants pose new challenges not encountered in typical applications of localized pollution. For example, what is an appropriate reference site (i.e., non-polluted site) for regionally dispersed pollutants transported through the atmosphere? Also, how can a pollutant exposure of effect be specifically attributed to an atmospheric source? Each of these considerations will be discussed briefly.

Attributing Exposure to Airborne Toxicants

Although airborne toxicants warrant concern because of the large scale dispersion that is possible with atmospherically transported material, the pollutants can enter specific ecosystems through a plethora of routes, including deposition of chemicals in water and soil, by entry into food chains, or by respiration of the air. Thus, identification of a pollutant at a site as atmospherically derived will probably depend on (1) chemical transport models and/or atmospheric tracer experiments; (2) direct measurement of chemical concentrations in environmental media, with an evaluation of whether the presence or concentration could be accounted for by other sources of environmental contamination (e.g., an nearby industrial source); and/or (3) identification of marker compounds or a "fingerprint" consortia of chemicals that can be linked to an atmospheric input.

Clearly, the identification of specific biomarkers of toxicants in plants has been elusive. Virtually all variables identified as potential indicators have limitations and do not meet the criteria of Arndt (1970) and Darrall and Jager (1984) detailed above. The critical shortcoming is that of specificity, with various toxicants eliciting similar responses, and with many responses also triggered by environmental variables. There are, however, several variables that may be related, that can provide a clear indication of oxidant perturbation. Ethylene production increases following stress, with oxidants constituting a high degree of stress, via generation of free radicals. Ethylene stimulates phenol metabolism, by stimulating PAL, and PPO. Oxidant stress stimulates free radical scavenging systems, leading to an increase in activities of superoxide dismutase, catalase and peroxidase. A combination of these variables hold the most potential as general indicators of oxidant stress, but pinpointing the specific oxidant requires simultaneous environmental monitoring.

Although these methods are needed to identify the potential for a deleterious exposure, it is the biomarker monitoring that is capable of determining if the toxicants are bioavailable, and if exposure is sufficient to account for ecologically relevant effects.

Selection of a Suitable Reference Site

Ideally, the reference site should be ecologically identical to the suspect site in all characteristics other than the potential for exposure to toxicants. In the more typical application of biomarkers in monitoring (Loar et al., 1987a,b), biomarker responses of animals collected from a site impacted by an industrial discharge are compared to responses of animals from a similar stream with no known source of pollution. In the case of widely dispersed atmospheric toxicants, true reference sites may not exist in all cases.

Perhaps the most reasonable alternative is to define reference sites as those in which transport models and chemical measurements suggest low impact due to atmospheric or other sources of pollutant input, and that are characterized by stable, diverse ecosystems. Given the difficulty in defining an appropriate reference site, it is particularly important to consider indices of habitat quality, such as soil type, percent ground cover, and such, to provide data to statistically test the alternate hypotheses that habitat or other environmental variables are responsible for any observed differences in biomarker responses between sentinel populations for two sites.

Linking Exposure and Effects

Conceptually, the biomarker-based monitoring approach develops evidence, and can statistically test hypotheses about the linkage between exposure to toxic chemicals and ecologically relevant effects. The rationale for the approach is indicated in Figure 5, which illustrates the relationship between responses at different levels of biological organization and the relevance and time scales of the responses. Responses at the population and community level are highly relevant to ecological concerns, but are slow to respond, and are difficult to attribute unequivocally to toxicants. In contrast, responses at lower levels of organization occur in shorter time frames and can be more clearly linked to toxic exposure; however, it is difficult to relate these responses to effects at the population and community level. Our approach is to measure responses at several different levels of biological organization, including metrics both of exposure to toxicants (generally responses in the upper left quadrant of Figure 5, but also including tissue burdens of chemicals) and of effects (generally the lower right quadrant). The goal in examining responses at these different levels of organization is to answer the following two critical questions.

1. Are organisms exposed to levels of toxicants that exceed the capacity of normal detoxication and repair systems?

2. If there is evidence of exposure, then is the chemical stress impacting the integrity of the populations or communities?

Evidence of exposure from body burdens or from responses at lower levels of biological organization provide an answer to the first question. In particular, the biomarkers of exposure indicate the biological significance of chemicals that may have entered the animal or plant (i.e., did the chemical reach molecular and biochemical targets and cause detectable damage, or induce a protective response?). The second question can be addressed by determining whether the responses to the toxicants is propagated up through successively higher levels of biological organization (biomarkers of effects and population parameters). If chemical exposure is responsible for a high level ecological effect, responses should be apparent at intermediate levels of organization.

Alternately, if the data do not indicate any evidence of exposure, or if biomarker responses indicate only minor effects in the most sensitive and responsive exposure parameters (e.g., genetic damage), but not at any higher levels of biological organization (e.g., histopathological evidence of neoplasia or tumors, or reduction in photosynthesis), community and population level effects could not be reasonably attributed to chemical agents. For this reason, any assessment approach also

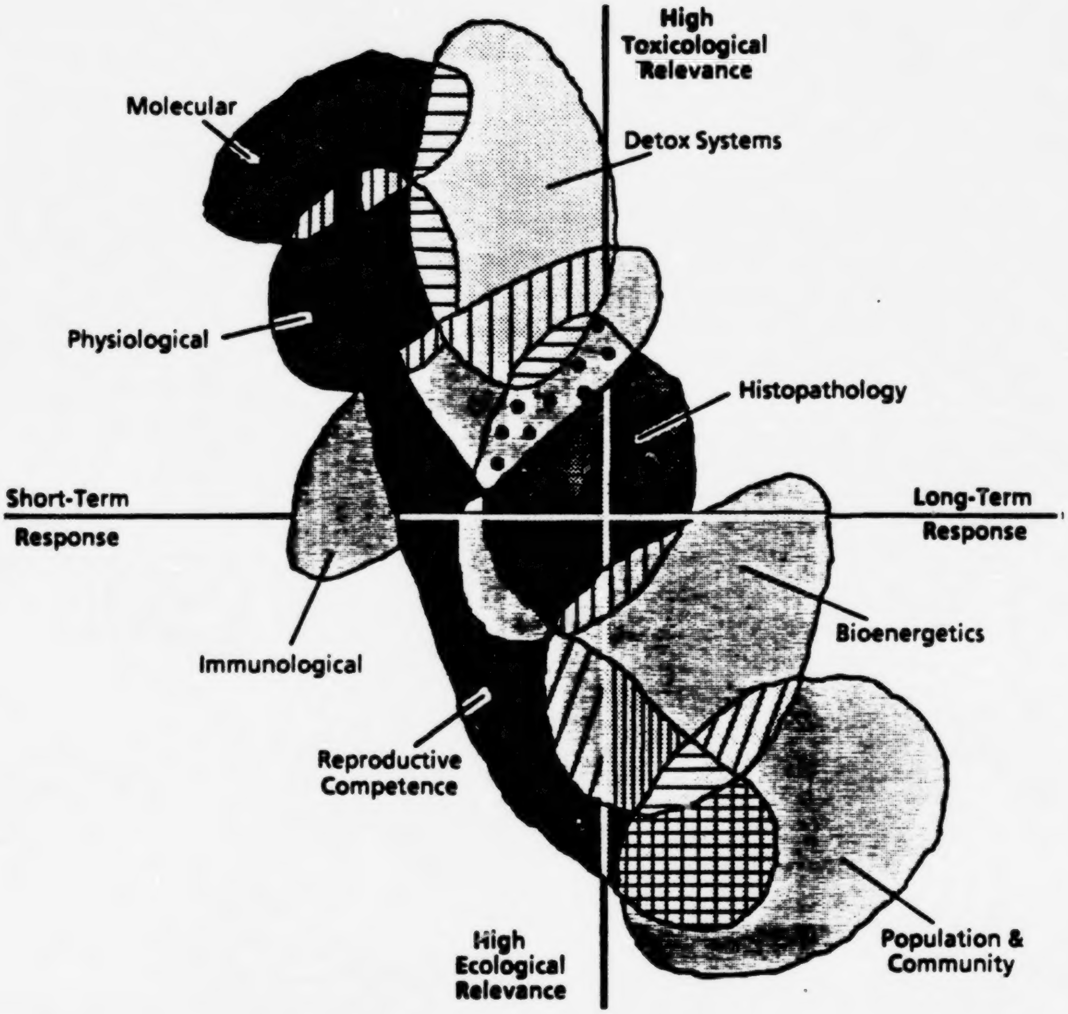
High
Toxicological
Relevance
Molecular
Detox Systems
Physiological
Histopathology
Short-Term
Response
Long-Term
Response
Immunological
Bioenergetics
Reproductive
Competence
Population &
Community
High
Ecological
Relevance

FIGURE 5. The relationship between responses at levels of biological organization and the relevance and time scales of responses.

needs to examine alternate hypotheses for ecological effects. For example, indices of habitat quality can be correlated with the population monitoring parameters to determine whether physical disturbance, or other measures of habitat quality, are better predictors of ecological response than are measurements of environmental concentrations of known toxicants, or the exposure parameters. If the biomarker data indicate that some level of toxic effect is occurring, but population parameters are better predicted by physical use or habitat quality, then multivariate statistics (Adams et al., 1985; Johnson, 1988) can be used to determine whether effects of chemicals are significantly contributing to the observed population response.

If a relationship is established between the chemical exposure and ecological effects, then the statistical models relating atmospheric sources to exposure and effects should be useful for estimating the extent and magnitude of existing effects, and to project the effect of continued releases.

ACKNOWLEDGEMENTS

We thank G. E. Taylor, N. Edwards and T. Moser for reviewing this manuscript. This work was supported by the Exploratory Studies Program, Oak Ridge National Laboratory, by the Oak Ridge Y-12 Plant, Division of Environmental Management, Health and Safety, and by the Biofuels and Municipal Waste Technology Division, U.S. Dept. Energy. TJT was supported by an appointment to the U.S. Dept. of Energy Postgraduate Research Program administered by Oak Ridge Associated Universities. The Oak Ridge Y-12 Plant and the Oak Ridge National Laboratory are operated by Martin Marietta Energy Systems, Inc., under contract DE-AC05-840R21400 with the U.S. Dept. of Energy. Publication No. 3661, Environmental Sciences Division, Oak Ridge National Laboratory.

AIR TOXICS ECOLOGICAL EFFECTS RESEARCH RECOMMENDATIONS

Noel R. Urban[1], and Jerry R. Barker[2]

[1]Environmental Engineering Sciences, University of Minnesota, Minneapolis, MN
[2]ManTech Environmental Technology, Inc., U.S. EPA Environmental Research Lab., Corvallis, OR

Nearly 65,000 chemicals are commonly used worldwide for industrial, agricultural, and domestic purposes (Schroeder and Lane, 1988). Many of these chemicals eventually are emitted directly or indirectly into the atmosphere as waste products. The airborne chemicals may then be transported and/or transformed through atmospheric processes and deposited into remote natural ecosystems as well as rural and urban environments. Airborne toxic chemicals can produce adverse effects ranging from the biochemical level to ecosystem structure and function. However, not all airborne chemicals pose the same magnitude of threat to biota and ecosystems. Therefore, research is needed to prioritize and rank pollutants according to their toxicity, ecological risk, and potential for human food-chain contamination. Research is also needed to document the spatial extent and magnitude of air toxics deposition, exposure to biota, and the resulting ecological effects.

Any research directed at assessment of the impacts of air pollution on ecosystems is confronted with several major problems. These include (but are not limited to): (1) an absence of background data to define the baseline from which change may be detected, and to determine the natural variability in ecosystem properties; (2) the existence of geographic gradients in ecosystem properties that confound efforts to compare impacted and nonimpacted regions; (3) the absence of systems free from contamination by air pollution, and the impracticality of maintaining ecosystem-scale exclosures; and (4) the existence of natural processes that mimic the effects of pollutants.

There are approaches to identifying changes induced by air toxics in any type of ecosystem that minimize the above stated problems. Integral components of a comprehensive approach are long-term monitoring at a few selected sites, periodic surveys, and process-oriented studies of contaminant fate and effects. Long-term monitoring and effects research are required to obtain baseline data on rates of important processes, on sizes and dynamics of populations, and environmental reservoirs. Paleoecological studies, such as chemical markers in ice and peat cores, provide a valuable extension of this monitoring into the past to document natural background concentrations. Because of the tremendous temporal variability in many ecosystem properties, periodic surveys are inadequate, and long-term monitoring is critically important for examining temporal trends. It is particularly important to monitor the rate of atmospheric deposition of contaminants. Simple measurements of input rates and pool sizes can give important indications of the mobility and persistence of contaminants. Since single sites are never adequately representative of a given ecosystem type, periodic surveys are required to evaluate variability in ecosystem properties and to examine spatial trends. It is critically important to consider natural gradients in ecosystem characteristics when regional surveys are used to compare the ecological responses of polluted and nonpolluted areas. Analysis of ecosystem responses across the short-distance gradients of pollutant exposure that surround many point-sources of air pollutants has been under-utilized in the past (Gorham and Gordon, 1963; Gignac and Beckett, 1986). At best, however, monitoring and surveys can only reveal correlations; they cannot prove causality or reveal mechanisms. Therefore, process-oriented studies that include laboratory and field manipulations are essential for proof of causality, elucidation of transport and transformation pathways, and anything more than empirical prediction of contaminant effects.

It is not a lack of vision into research needs that impedes progress, for these recommendations are far from new. Nevertheless, there is no ongoing national monitoring of atmospheric deposition of trace metals, synthetic organic chemicals, and other air toxics. There is also no ongoing monitoring of contaminant cycling in terrestrial and aquatic ecosystems and there is very little baseline data on fundamental ecosystem processes (Kelly and Harwell, 1982). Very little of the ongoing process-oriented research in terrestrial and aquatic ecosystems is directed at the ecological risk assessment of air toxics effects.

REFERENCES

Aaby, B., and J. Jacobsen. Changes in biotic conditions and metal deposition in the last millennium as reflected in ombrotrophic peat in Draved Mose, Denmark. Danm. Geol. Unders. Arbog., 1978, 00. 5-43, 1979.

Abbott, D.C., R.B. Harrison, J. O'G. Tatton, and J. Thomson. Organochlorine pesticides in the atmosphere. Nature, 211:259-261, 1966.

Abeles, F.B. Ethylene in Plant Biology. Academic Press. New York. ISBN 0-12-041450-3. 1973.

Aberg, E., and V. Stecko. Internal factors affecting toxicity. In: L.J. Audus (ed.). Herbicides: Physiology, Biochemistry, Ecology. Vol. 2. Academic Press, London, 1976. pp. 175-203.

Adams, S.M., C.A. Burtis, and J.J. Beauchamp. Integrated and individual biochemical responses of rainbow trout (*Salmo gairdneri*) to varying durations of acidification stress. Comp. Biochem. Physiol., 82:301-310, 1985.

Adams, D.F., and S.O. Farwell. Biogenic sulfur source strengths. Environ. Sci. Technol., 15:1493-1498, 1981.

Addicott, F.T. Actions on abscission, defoliation and related respones. In: L.J. Audus (ed.). Herbicides: Physiology, Biochemistry, Ecology. Vol. 1. Academic Press, London, 1976. pp. 191-219.

Addison, R.F., and M.E. Zinck. PCBs have declined more than DDT-group residues in Arctic ringed seals (*Phoca hispida*) between 1972 and 1981. Environ. Sci. Technol., 20:253-256, 1986.

Adriano, D.C. Trace Elements in The Terrestrial Environment. Springer-Verlag, New York, Chapters 1,7,9,1, 1986.

Adriano, D.C., D.I. Kaplan, W.G. Burkman, and G.L. Mills. Long-term phytoavailability of soil-applied organo-borates. J. Environ. Qual., 17:485-492, 1988.

Agarwal, H.C., C.P. Kaushik, and M.K.K. Pillai. Organochlorine insecticide residues in the rain water in Delhi, India. Water, Air, and Soil Pollut., 32:293-302, 1987.

Alstrup, V., and E.S. Hansen. Three species of lichens tolerant of high concentrations of copper. Oikos, 29:290-293, 1977.

Alvares, A.P., G. Schilling, W. Levin, and R. Kuntzman. Studies on the induction of CO-binding pigments in the liver microsomes by phenobarbital and 3-methylcholanthrene. Biochem. Biophys. Res. Commun., 29:521-526, 1967.

Amer, S., and E.M. Ali. Effects of phenols on the plant. Beitr. Biol. Pflanz., 44:59-65, 1968.

Amer, S., and E.M. Ali. Cytological effects of pesticides. IV. Mitotic effects of some phenols. Cytologia, 34:533-540, 1969.

Andelman, J.B., and M.J. Suess. Polynuclear aromatic hydrocarbons in the water environment. Bull. WHO, 43:479-508, 1970.

Andresen, A.M., A.H. Johnson, and T.G. Siccama. Levels of lead, copper, and zinc in the forest floor in the northeastern United States. J. Environ. Qual., 9:293, 1980.

Aranda, J.M., G.A. O'Connor, and G.A. Eiceman. Effects of sewage sludge on di-(2-ethylhexyl) pthatlate uptake by plants. J. Environ. Qual., 18:45-50, 1989.

Arndt, U. Konzentrationsanderungen bei Freien Aminosauren in Pflanzen unter dem Einfluss von Fluorwasserstoff und Schwefeldioxid. Staub-Reinhalt. Luft. 36:256-259, 1970.

Arp, P.A., and R. Ouimet. Uptake of Al, Ca, and P in black spruce seedlings: effect of organic versus inorganic Al in nutrient solutions. Water, Air, and Soil Pollut., 31:367-376, 1986.

Ashton, F.M., and D.E. Bayer. Effects on solute transport and plant constituents. In: L.J. Audus (ed.). Herbicides: Physiology, Biochemistry, Ecology. Vol. 1. Academic Press, London, 1976. pp. 220-254.

Atlas, E., R. Foster, and C.S. Giam. Air-sea exchange of high molecular weight organic pollutants: laboratory studies. Environ. Sci. Technol., 16(5):283-286, 1982.

Atlas, E., and C.S. Giam. Global transport of organic pollutants: ambient concentrations in the remote marine atmosphere. Science, 20:163-165, 1981.

Atlas, E., and C.S. Giam. Ambient concentration and precipitation scavenging of atmospheric organic pollutants. Water, Air, and Soil Pollut., 38:19-36, 1988.

Atlas, E., and C.S. Giam. Sea-air exchange of high molecular weight synthetic organic compounds: Results from the SEAREX program. In: J.P. Riley, R. Chester and R.A. Duce (eds.). Chemical Oceanography, 10, 1989.

Aulio, K. The effects of sulphuric compounds on the ATP content of the peat moss *Sphagnum fuscum*. Chemosphere, 13:915-918, 1984.

Bacci, E., and C. Gaggi. Polychlorinated biphenyls in plant foliage: translocation or volatilization from contaminated soils? Bull. Environ. Contam. Toxicol., 35:673-681, 1985.

Bacci, E., D. Calamari, C. Gaggi, R. Fanelli, S. Focardi, and M. Morosini. Chlorinated hydrocarbons in lichen and moss samples from the Antarctic peninsula. Chemosphere, 15:747, 1986.

Baker, J.M. The effects of oils on plants. Environ. Pollut., 1:27-44, 1970.

Barber, D.A., and H.B. Koontz. Uptake of dinitrophenol and its effect on transpiration and calcium accumulation in barley seedlings. Plant Physiol., 38:60-65, 1963.

Bargagli, R., F.P. Iosco, and C. Barghigiani. Assessment of mercury dispersal in an abandoned mining area by soil and lichen analysis. Water, Air, and Soil Pollut., 36:219-225, 1987.

Barrie, L.A. Arctic air pollution: an overview of current knowledge. Atmos. Environ., 20:643-663, 1986.

Baxter, R., M.J. Emes, and J.A. Lee. Effects of the bisulphite ion on growth and photosynthesis in *Sphagnum cuspidatum* Hoffm. New Phytol., 111:457-462, 1989a.

Baxter, R., M.J. Emes, and J.A. Lee. The relationship between extracellular metal accumulation and bisulphite tolerance in *Sphagnum cuspidatum* Hoffm. New Phytol., 111:463-472, 1989b.

Bayley, S.E., R.S. Behr, and C.A. Kelly. Retention and release of S from a freshwater wetland. Water, Air, and Soil Pollut., 31:101-114, 1986.

Bayley, S., and D.W. Schindler. Sources of alkalinity in PreCambrian shield watersheds under natural conditions and after fire or acidification. In: T.C. Hutchinson and K. Meems (eds.). Effects of Air Pollutants on forests and wetlands. Springer-Verlag, NY, 1987. pp. 531-548

Bayley, S.E., D.H. Vitt, R.W. Newbury, K.G. Beaty, R. Behr, and C. Miller. Experimental acidification of a *Sphagnum*-dominated peatland: first year results. Can. J. Fish, Aquat. Sci., 44:194-205, 1987.

Beall, M.L., and R.G. Nash. Organochlorine insecticide residues in soybean and plant tops: root uptake vs. vapor sorption. Agron. J., 63:460-464, 1971.

Beckett, P.J., L.J.R. Boileau, D. Padovan, and D.H.S. Richardson. Lichens and mosses as monitors of industrial activity associated with uranium mining in northern Ontario, Canada, Part 2, distance dependent uranium and lead accumulation patterns. Environ. Pollut., 4:91-107, 1982.

Beevers, H. 2,4-dinitrophenol and plant respiration. Am. J. Bot., 40:91-96, 1953.

Behr, R.S. Sulfur dynamics in an experimentally acidified mire in northwestern Ontario. M.S. Thesis, University of Manitoba, 1985. 105 pp.

Behrens, R., and W.E. Lueschen. Dicamba volatility. Weed Sci., 27:486, 1979.

Bellamy, D.J., and J. Riely. Some ecological statistics of a miniature bog. Oikos, 18:33-40, 1967.

Bend, J.R., and M.O. James. Xenobiotic metabolism in marine and freshwater species. Biochem. Biophys. Perspec. Mar. Biol., 4:125-188, 1979.

Bennett, J.H., E.H. Lee, and H.E. Heggestad. Biochemical aspects of plant tolerance to ozone and oxyradicals: superoxide dismutase. In: M.J. Koziol and F.R. Whatley (eds.). Gaseous Air Pollutants and Plant Metabolsim. Butterworths, London. ISBN 0-408-11152-6, 1984.

Bidleman, T.F. Atmospheric processes: wet and dry deposition of organic compounds are controlled by their vapor-particle partitioning. Environ. Sci. Technol., 22(4):361-367, 1988.

Bidleman, T.F., and E.J. Christensen. Atmospheric removal processes for high-molecular-weight organochlorines. J. Geophys. Res., 84:7857-7862, 1979.

Bidleman, T.F., G.W. Patton, M.D. Walla, B.T. Hargrave, W.P. Vass, P. Erickson, B. Fowler, V. Scott, and D.J. Gregor. Toxaphene and other organochlorines in the Arctic Ocean. Arctic, 42:307-313, 1989.

Bidleman, T.F., G.W. Patton, D.A. Hinckley, M.D. Walla, W.E. Cotham, and B.T. Hargrave. Chlorinated Pesticides and Polychlorinated Biphenyls in the Atmosphere of the Canadian Arctic. In: D.A. Kurtz (ed.). Long-Range Transport of Pesticides. Lewis Publishers, Chelsea, MI, 1990.

Bidleman, T.F., U. Wideqvist, B. Jansson, and R. Soderlund. Organochlorine pesticides and polychlorinated biphenyls in the atmosphere of southern Sweden. Atmos. Environ., 21:641-654, 1987.

Billings, W.N., and T.F. Bidleman. High volume collections of chlorinated hydrocarbons in urban air using three solid adsorbents. Atmos. Environ., 17:383-391, 1983.

Birkeland, P.W. Soils and Geomorphology. Oxford University Press, New York, Chapter 7, 1984.

Blancher, P.J., and D.K. McNichol. Peatland water chemistry in central Ontario in relation to acid deposition. Water, Air, and Soil Pollut., 35:217-232, 1987.

Blankenship, D.W., and R.A. Larson. Plant growth inhibition by the water extract of a crude oil. Water, Air, and Soil Pollut., 10:471-476, 1978.

Blokzijl, P.J., and R. Guicherit. The occurrence of polynuclear aromatic hydrocarbons (PAH) in outdoor air. TNO-Nieuws, 27:653-660, 1972.

Blumer, M. Benzopyrenes in soil. Science, 134:474-475, 1961.

Boersma, L., F.T. Lindstrom, C. McFarlane, and E.L.McCoy. Uptake of organic chemicals by plants: a theoretical model. Soil Sci., 146:403-417, 1988.

Boileau, L.J.R., P.J. Beckett, P. Lavoie, D.H.S. Richardson, and E. Nieboer. Lichens and mosses as monitors of industrial activity associated with uranium mining in northern Ontario, Canada. 1. Field procedures, chemical analysis and inter-species comparisons. Environ. Pollut., 4:69-84, 1982.

Borneff, F., H. Selenka, H. Kunte, and A. Maximos. The synthesis of 3,4-benzopyrene and other polycyclic aromatic hydrocarbons in plants. Arch. Hyg., 152:279-282, 1968a.

Borneff, F., H. Selenka, H. Kunte, and A. Maximos. Experimental studies on the formation of polycyclic aromatic hydrocarbons in plants. Environ. Res., 2:22-29, 1968b.

Boucher, V.L., and T.H. Nash III. The role of the fruticose lichen *Ramalina menziesii* in the annual turnover of biomass and macronutrients in a blue oak woodland. Bot. Gaz., 151:114-118, 1990.

Bourget, S.J., and E.V. Parups. Growth of tobacco an soil-moisture evaporation as influenced by lon-chain fatty alcohols in the soil. Soil Sci., 95:82-85, 1963.

Boutron, C.F., and C.C. Patterson. The occurrence of lead in Antarctic recent snow, firn deposited over the last two centuries and prehistoric ice. Geochim. Cosmochim. Acta., 47:1355-1368, 1983.

Bowden, W.B. Nitrification, nitrate reduction, and nitrogen immobilization in a tidal freshwater marsh sediment. Ecology, 67:88-99, 1986a.

Bowden, W.B. Gaseous nitrogen emissions from undisturbed terrestrial ecosystems: an assessment of their impacts on local and global nitrogen budgets. Biogeochem., 2:249-279, 1986b.

Bowden, W.B. The biogeochemistry of nitrogen in freshwater wetlands. Biogeochem., 4:313-332, 1987.

Bowes, G.W., and C.J. Jonkel. Presence and distribution of polychlorinated byphenyls (PCB) in Arctic and sub-Arctic marine food chains. Can. J. Fish Aquat. Sci., 32:2111-2123, 1975.

Braekke, F.H. Hydrochemistry of high altitude catchments in south Norway, 1. Effects of summer droughts and soil vegetation characteristics. Rep. Norw. For. Res. Inst., 36.8:26, 1981.

Brennan, E.G., I.A. Leone, and R.H. Daines. Atmospheric aldehydes related to Petunia leaf damage. Science, 143:818-820, 1964.

Bressan, R.A., L. LeCureux, L.G. Wilson, and P. Filner. Emission of ethylene and ethane by leaf tissue exposed to injurious concentrations of sulphur dioxide or bisulphite ions. Plant Physiol., 63:924-930, 1979.

Briggs, G.G., R.H. Bromilow, and A.A. Evans. Relationship between lipophilicity and root uptake and translocation of non-ionized chemicals by barley. Pesticide Sci., 13:495-504, 1982.

Briggs, G.G., R.H. Bromilow, A.A. Evans, and M. Williams. Relationships between lipophilicity and the distribution of non-ionized chemicals in barley shoots following uptake by the roots. Pesticide Sci., 14:492-500, 1983.

Brown, D.H., and R.P. Beckett. Differential sensitivity of lichens to heavy metals. Ann. Bot., 52:51-57, 1983.

Bruckmann, P., W. Kersten, W. Funcke, E. Balfanz, J. Konig, J. Theisen, M. Ball, and O. Papke. The occurrence of chlorinated and other organic trace compounds in urban air. Chemosphere, 17:2363-2380, 1988.

Buckley, E.H. Accumulation of airborne polychlorinated biphenyls in foliage. Science, 216:520-522, 1982.

Buckauer, M. J. Contamination of soil and vegetation near a Zn smelter by Zn, Cd, Cu, and Pb. Environ. Sci. Technol., 7:131-135, 1973.

Budimir, M., M. Lesniar, and R. Kljacjic. Effects of the herbicide 2,4-DB and fungicide captan on reactions of mitochondria and chloroplasts. Arch. Environ. Contam. Toxicol., 4:166-174, 1976.

Bukovac, M.J. Herbicide entry into plants. In: L.J. Audus (ed.). Herbicides: Physiology, Biochemistry, Ecology. Vol. 1. Academic Press, London, 1976. pp 335-364.

Burkhard, L.P., D.E. Armstrong, and A.W. Andren. Henry's Law constants for the polychlorinated biphenyls. Environ. Sci. Technol., 19(7):590-596, 1985.

Buta, J. G. Plant growth regulating activity of substituted pthalate esters. J. Agric. Food Chemistry, 23:801-802, 1975.

Calleman, C.J. Hemoglobin as a dose monitor and its application to risk estimation of ethylene oxide. Dept. of Radiobiology, Univ. of Stockholm, Stockholm, Sweden, 1984.

Caro, J.H., A.W. Taylor, and H.P. Freeman. Comparative behavior of dieldrin and carbofuran in the field. Arch. Environ. Contam. Toxicol., 3:437-447, 1976.

Cartwright, P.M. General growth responses of plants. In: L.J. Audus (ed.). Herbicides: Physiology, Biochemistry, Ecology. Vol. 1. Academic Press, London, 1976. pp. 55-126.

Casterline, J.L., Jr., Y. Ku, and N.M. Barnett. Uptake of tri-p-cresyl phosphate in soybean plants. Bull. Environ. Contam. Toxicol., 35:209-212, 1985.

Castillo, F.J., P.R. Miller, and H. Greppin. Extracellular biochemical markers of photochemical oxidant air pollution damage to Norway spruce. Experientia, 43:111-115, 1987.

Cataldo, D.A., R.E. Wildung, and T.R. Garland. Speciation of trace inorganic contaminants in plants and bioavailability to animals: an overview. J. Environ. Qual., 16:289, 1987.

Chamberlain, A.C. The movement of particles in plant communities. In: J.L. Monteith (ed.). Vegetation and the Atmosphere. Vol. 1: Principles. Academic Press, New York, 1975. pp. 155-203.

Chambers, J.E., and J.D. Yarbrough. Xenobiotic biotransformation systems in fishes. Comp. Biochem. Physio., 55C:77-84, 1976.

Chameides, W.L., R.W. Lindsay, J. Richardson, and C.S. Kiang. The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study. Science, 241:1473-1475,1988.

Chapman, E.G., D.S. Sklarew, and J.S. Flickinger. Organic acids in springtime Wisconsin precipitation samples. Atmos. Environ., 20:1717-1725, 1986.

Cherry, J.H. Actions on nucleic acid and protein metabolism. In: L.J. Audus (ed.). Herbicides: Physiology, Biochemistry, Ecology. Vol. 1. Academic Press, London, 1976. pp. 525-546.

Chevreuil, M., A. Chesterikoff, R. Letolle, and L. Granier. Atmospheric pollution and fallout by PCBs and organochlorine pesticides (Ile-de-France). Water, Air, and Soil Pollut., 43:73-83, 1989.

Christensen, E.J., C.E. Olney, and T.F. Bidleman. Comparison of dry and wet surfaces for collecting organochlorine dry deposition. Bull. Environ. Contam. Toxicol., 23:196-202, 1979.

Cleland, J.G. Environmental Hazard Rankings of Pollutants Generated in Coal Gasification Processes. US EPA Project Summary. EPA-600/57-81-101. Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina, 1981. 19 pp.

Clymo, R.S. Interactions of *Sphagnum* with water and air. In: T.C. Hutchinson and K. Meema (eds.). Effects of Air Pollutants on Forests, Agriculture and Wetlands. Spring-Verlag, NY, 1987, pp. 513-530.

Clymo, R.K., and P.M. Hayward. The ecology of *Sphagnum*. In: A.J.E. Smith (ed.). Bryophyte Ecology. Chapman and Hall, London, 1982, pp. 229-289.

Cohen, Y. Organic pollutant transport. Environ. Sci. Technol., 20:538-544, 1986.

Cohen, M.L., and W.D. Steinmetz. Foliar washoff of pesticides. Environ. Sci. Technol., 20:521-523, 1986.

Coker, W.B., and R.N.W. Dilabio. Initial geochemical results and exploration significance of two uraniferous peat bogs, Kasmere Lake, Manitoba. In: Current Res. Part B. Geol. Survey of Canada. Paper 79-aB. 1979, pp. 199-206.

Collins, C.R., and J.F. Farrar. Structural resistances to mass transfer in the lichen *Xanthoria parietina*. New Phytol., 81:71-83, 1978.

Crafts, A.S., and H.G. Reiber. Herbicidal properties of oils. Hilgardia, 18:77-156, 1948.

Crerar, D.A., G.W. Knox, and J.L. Means. Biogeochemistry of bog iron in the New Jersey Pine Barrens. Chem. Geol., 24:111-135, 1979.

Currier, H.B. Herbicidal properties of benzene and certain methyl derivatives. Hilgardia, 20:383-406, 1951.

Currier, H.B., and S.A. Peoples. Phytotoxicity of hydrocarbons. Hilgardia, 23:155-173, 1954.

Daisey, J.M., R.J. McCaffrey, and R.A. Gallagher. Polycyclic aromatic hydrocarbons and total extractable particulate matter in the Arctic aerosol. Atmos. Environ., 15:1353-1363, 1981.

Daniel, F.B., D.L. Haas, and S.M. Pyle. Quantitation of chemically induced DNA strand breaks in human cells via an alkaline unwinding assay. Anal. Biochem., 144:390-402, 1985.

Daroczy, S., A. Bolyos, Z. Dezso, A. Pazsit, and J. Nagy. Could mosses be used for the subsequent mapping of the Chernobyl fallout? Naturwiss., 75:569-570, 1988.

Darrall, N.M., and H.J. Jager. Biochemical diagnostic tests for the effect of air pollution on plants. In: M.J. Koziol and F.R. Whatley (eds.). Gaseous Air Pollutants and Plant Metabolism. Butterworths. London. ISBN 0-408-11152-6, 1984.

Davidson, C.I., W.D. Goold, T.P. Mathison, G.B. Wiersma, K.W. Brown, and M.T. Reilly. Airborne trace elements in Great Smoky Mountains, Olympic, and Glacier National Parks. Environ. Sci. Technol., 19:27, 1985.

Davidson, C.I., T.C. Grimm, and M.A. Nasta. Airborne lead and other elements derived from local fires in the Himalayas. Science, 214:1344, 1981.

Deubert, K.H., R.M. Devlin, M.J. Kisiel, and A.S. Kostusiak. The influence of benzo[a]pyrene on the growth of wheat and corn. Environ. Int., 2:91-93, 1979.

DeWailly, E., A. Nantel, J.P. Weber, and F. Meyer. High level of PCBs in breast milk in Inuit women in Arctic Quebec. Bull. Environ. Contam. Toxicol., 43:641, 1989.

Dörr, R. Absorption of 3,4-benzopyrene by plant roots. Landwirtsch. Forsch., 23:371-379, 1970. (English translation--ORNL/TM-4122. Oak Ridge National Laboratory, Oak Ridge, Tennessee).

Downton, W.J.S., and E.B. Tregunna. Photorespiration and glycolate metabolism: a re-examination and correlation of some previous studies. Plant Physiol., 43:923-929, 1968.

Duce, R.A., R. Arimoto, B.J. Ray, C.K. Unni, and P.J. Harder. Atmospheric trace elements at Enewetak Atoll: concentrations, sources, and temporal variability. J. Geophys. Res., 88:5321-5342, 1983.

Duke, J.A. Phytotoxin tables. CRC Crit. Rev. Toxicol., 5:189-238, 1977.

Duinker, J.C. and F. Bouchertall. On the distribution of atmospheric polychlorinated biphenyl congeners between vapor phase, aerosols, and rain. Environ. Sci. Tech., 23:57-62, 1989.

Edgerton, S.A., M.W. Holdren, D.L. Smith, and J.J. Shah. Inter-urban comparison of ambient volatile organic compound concentrations in U.S. cities. J. Air Pollut. Control Assoc., 39:729-732, 1989.

Edgington, D.N., and J.A. Robbins. Records of lead deposition in Lake Michigan sediments since 1800. Environ. Sci. Technol., 10:266-274, 1976.

Edwards, N.T. Polycyclic aromatic hydrocarbons (PAHs) in the terrestrial environment: a review. J. Environ. Qual., 12:427-441, 1983.

Edwards, N.T. Uptake, translocation and metabolism of anthracene in bush bean (*Phaseolus vulgaris* L.). Environ. Toxicol. Chem., 5:659-665, 1986.

Edwards, N.T., R.M. Ross-Todd, and E.G. Garver. Uptake and metabolism of ^{14}C anthracene by soybean (*Glycine max*). Environ. Exp. Bot., 22:349-357, 1982.

Eger, P., K. Lapakko, and P. Otterson. Trace metal uptake by peat: interaction of a white cedar bog and mining stockpile leachate. In: Proc. 6th Int. Peat Congr. Duluth, MN, USA, 1981. pp. 542-547.

Eisenreich, S.J. The chemical limnology of nonpolar organic contaminants: polychlorinated biphenyls in Lake Superior. In: R.A. Hites and S.J. Eisenreich (eds.). Sources and Fates of Aquatic Pollutants. Amer. Chem. Soc. Washington, DC, 1987. pp. 393-470.

Eisenreich, S.J., B.B. Looney, and J.D. Thornton. Airborne organic contaminants in the Great Lakes ecosystem. Environ. Sci. Technol., 15:30-38, 1981.

Elder, J., R. Ginsburg, D. Miller, and C. Davis. Sweet water, bitter rain: toxic air pollution in the Great Lakes Basin. Sierra Club, San Francisco, California. 1988.

Ellwardt, P. Symposium on Soil Organic Matter Studies, Vol. II. IAEA, Vienna, 1977. pp. 291-298.

Eriksson, G., S. Jensen, H. Kylin, and W. Strachan. The pine needle as a monitor of atmospheric pollution. Nature, 341:42-44, 1989.

Evans, W.C., H.N. Fernley, and E. Griffiths. Oxidative metabolism of phenanthrene and anthracene by soil pseudomonads. Biochem. J., 95:819-831, 1965.

Facchetti, S., A. Balasso, C. Fichtner, G. Frare, A. Leoni, C. Mauri, and M. Vasconi. Studies on the absorption of TCDD by some plant species. Chemosphere, 15:1387, 1986.

Farmer, C.T., and T.L. Wade. Relationship of ambient atmospheric hydrocarbon (C_{12}- C_{14}) concentrations to deposition. Water, Air, and Soil Pollut., 29:439-452, 1986.

Fendlinger, N.J., and D.E. Glotfelty. A laboratory method for the experimental determination of air-water Henry's Law constants for several pesticides. Environ. Sci. Technol., 22(11):1289-1293, 1988.

Ferguson, P., J.A. Lee, and J. Bell. Effects of sulfur pollutants on the growth of *Sphagnum* species. Environ. Pollut., 16:151-162, 1978.

Ferguson, P., and J.A. Lee. Some effects of bisulfite and sulfate on the growth of *Sphagnum* species in the field. Environ. Pollut., 21:59-71, 1980.

Ferguson, P., and J.A. Lee. Past and present sulphur pollution in the southern Pennines. Atmos. Environ., 17:1131-1137, 1983a.

Ferguson, P., and J.A. Lee. The growth of *Sphagnum* species in the southern Pennines. J. Bryol., 12:579-586, 1983b.

Ferguson, P., R.N. Robinson, M.C. Press, and J.A. Lee. Element concentrations in five *Sphagnum* species in relation to atmospheric pollution. J. Bryol., 13:107-114, 1984.

Fernandez, I.J., and M.M. Czapowsky. Levels of trace metals in the forest floors of low elevation, commercial spruce-fir sites in Maine. Northeast Environ. Sci., 4:107, 1985.

Fletcher, J.S., F.L. Johnson, and J.C. McFarlane. Database assessment of phytotoxicity data published on terrestrial vascular plants. Environ. Toxicol. Chem., 7:615-622, 1988.

Fletcher, J.S., F.L. Johnson, and J.C. McFarlane. Influence of greenhouse versus field testing and taxonomic differences on plant sensitivity to chemical treatment. Environ. Toxicol. Chem., 9:769, 1990.

Fletcher, J.S., J.C. McFarlane, T. Pfleeger, and C. Wickliff. Influence of root exposure concentration on the fate of nitrobenzene in soybean. Chemosphere, 20:513-523, 1990.

Fogg, G.E. The penetration of 3:5-dinitro-o-cresol into leaves. Appl. Biol., 35:21-330, 1948.

Folkeson, L. Heavy-metal accumulation in the moss *Pleurozium schreberi* in the surroundings of two peat-fired power plants in Finland. Ann. Bot. Fennici., 18:245-253, 1981.

Food and Agriculture Organization of the United Nations. Production Yearbooks. Vol. 31-39, Rome, Italy. 1978-86.

Food and Agricultural Organization of the United Nations. Production Yearbook. Vol. 39-40, Rome, Italy. 1986-87.

Foreman, W.T., and T.F. Bidleman. An experimental system for investigating vapor-particle partitioning of trace organic pollutants. Environ. Sci. Technol., 21:869-875, 1987.

Forrest, V., T. Cody, J. Caruso, and D. Warshawsky. Influence of the Carcinogenic Pollutant Benzo[a]pyrene on Plant Development: Fern Gametophytes. Chemico-Biological Interactions, 1989.

Fox, M.A., and S. Olive. Photooxidation of anthracene on atmospheric particulate matter. Science, 205:582-583, 1979.

Frank, H., and W. Frank. Chlorophyll-bleaching by atmospheric pollutants and sunlight. Naturwiss., 72:139-141, 1985.

Frank, H., and W. Frank. Photochemical activation of chloroethenes leading to destruction of photosynthetic pigments. Experientia, 42:1267-1269, 1986.

Frank, H., and W. Frank. Uptake of airborne tetrachlorethene by spruce needles. Environ. Sci. Technol., 23:365-367, 1989.

Fraser, D.C. Organic sequestration of copper. Economic Geol., 56:1063-1078, 1961.

Fridovich, I. Superoxide radical: an endogenous toxicant. Ann. Rev. Pharmacol. Toxicol., 23:239-257, 1983.

Friedland, A.J. The Movement of Metals Through Soils and Ecosystems. In: J. Shaw, ed. Heavy Metal Tolerance in Plants: Evolutionary Aspects, CRC Press, 1989.

Friedland, A.J., A.H. Johnson, T.G. Siccama, and D.L. Mader. Trace metal profiles in the forest floor of New England. Soil Sci. Soc. Am. J., 48:422, 1984a.

Friedland, A.J., A.H. Johnson, and T.G. Siccama. Trace metal content of the forest floor in the Green Mountains of Vermont: spatial and temporal patterns. Water, Air, and Soil Pollut., 21:161, 1984b.

Friedland, A.J., and A.H. Johnson. Lead distribution and fluxes in a high-elevation forest in northern Vermont. J. Environ. Qual., 14:332, 1985.

Friedland, A.J., A.H. Johnson, and T.G. Siccama. Zinc, Cu, Ni and Cd in the forest floor in the northeastern United States. Water, Air, and Soil Pollut., 29:233, 1986a.

Friedland, A. J., A.H. Johnson, and T.G. Siccama. Coniferous litter decomposition on Camels Hump, Vermont: a review. Can. J. Bot., 64:1349, 1986b.

Fries, G.F., and G.S. Marrow. Chlorobiphenyl movement from soil to soybean plants. J. Agric. Food Chem., 29:757-759, 1981.

Fritz, W. Extent and sources of contamination of our food with carcinogenic hydrocarbons. Ernaehrungsforsch., 16:547-557, 1971.

Frosch, S., J. Franzen, A. Tremolliere, and E. Wagner. β-pinene mediated rearrangement of fatty acids in lipid classes of spruce seedlings. In International Congress on Forest Decline Research: State of Knowledge and Perspectives. Forschungsbei[illegible] Waldschaden/Luftverunreinigungen der Bundesregierung und der Lander, Lake Constance, West Germany, 1989. pp. 441.

Furr, K., C. Schofield, M. Grandolfo, R. Hofstader, W. Gutenmann, L. St. John, and D. Lisk. Element content of mosses as possible indicators of air pollution. Arch. Environ. Contam. Toxicol., 8:335-343, 1979.

Gaffney, J.S., G. E. Streit, W.D. Spall, and J.H. Hall. Beyond acid rain. Environ. Sci. Technol., 21:519-524, 1987.

Galloway, J.N., J.D. Thornton, S.A. Norton, H.L. Volchok, and R.A. McLean. Trace metals in atmospheric deposition: a review and assessment. Atmos. Environ., 16:1677, 1982.

Garland, J.A., K.W. Nicholson, and R.G. Derwent. The deposition of trace substances from the atmosphere. In: K. Grefen and J. Lobel (eds.). Environmental Meteorology, UKAEA, 1988. pp. 141-160.

Garrett, W.D. Collection of slick-forming material from the sea surface. Limnol. Oceanogr., 10:602-605, 1965.

Garty, J., M. Galun, and M. Kessel. Localization of heavy metals and other elements accumulated in the lichen thallus. New Phytol., 81:159-168, 1979.

Gaur, B.K., and H. Beevers. Respiratory and associated responses of carrot discs to substituted phenols. Plant Physiol., 34:427-432, 1959.

Giam, C.S., E. Atlas, M.A. Powers, and J.E. Leonard. Phthalic acid esters. In: O. Hutzinger (ed.). The Handbook of Environmental Chemistry: Anthropogenic Compounds. Volume 3, Part C. Springer-Verlag, New York, 1984. pp. 67-142.

Gianessi, L.P., and C.A. Puffen. Use of Selected Pesticides in Agricultural Crop Production by State. Quality of the Environment Division. Resources for the Future, 1988.

Giblin, A.E., and R.K. Wieder. Sulfur cycling in saline and freshwater wetlands: a review. In: R.W. Howarth and J.W.B. Stewart (eds.). Sulfur Cycling in Terrestrial Systems and Wetlands. Wiley, New York, 1990.

Gibson, D.T., V. Mahadevan, D.M. Jerina, H. Yagi, and H.J.C. Yeh. Oxidation of the carcinogens benzo[a]pyrene and benzo[a]anthracene to dihydrodiols by a bacterium. Science, 189:295-297, 1975.

Gignac, L.D., and P.J. Beckett. The effect of smelting operations on peatlands near Sudbury, Ontario, Canada. Can. J. Bot., 64:1138-1147, 1986.

Gillen, R.L., D.R. Rollins, and J.F. Stritzke. Atrazine, spring burning, and nitrogen for improvement of tallgrass prairie. J. Range Manage., 40:444, 1987.

Glass, A.D.M. Influence of phenolic acids upon ion uptake. I. Inhibition of phosphate uptake. Plant Physiol., 51:1037-1041, 1973.

Glass, A.D.M. Influence of phenolic acids upon ion uptake. III. Inhibition of potassum absorption. J. Exp. Bot., 25:1104-1113, 1974.

Glime, J.M., R.G. Wetzel, and B.J. Kennedy. The effects of bryophytes on succession from alkaline marsh to *Sphagnum* bog. Am. Midland Naturalist., 108:209-223, 1982.

Glooschenko, W.A., and J.A. Capoblanco. Metal content of *Sphagnum* mosses from two northern Canadian bog ecosystems. Water, Air, and Soil Pollut., 10:215-220, 1978.

Glotfelty, D.E., M.M. Leech, J. Jersey, and A.W. Taylor. Volatilization and wind erosion of soil surface applied atrazine, simazine, alachlor, and toxaphene. J. Agric. Food Chem., 37:546, 1989.

Glotfelty, D.E., A.W. Taylor, B.C. Turner, and W.H. Zoller. Volatilization of surface applied pesticides from fallow soil. J. Agric. Food Chem., 32:638, 1984.

Glotfelty, D.E., J.N. Seiber, and L.A. Liljedahl. Pesticides in fog. Nature, 325:602-605, 1987.

Godish, T., and C. Guindon. An assessment of botanical air purification as a formaldehyde mitigation measure under dynamic laboratory chamber conditions. Environ. Pollut., 61:13-20, 1989.

Goodwin, T.W., and E.I. Mercer. Introduction to plant biochemistry. Pergamon Press. New York. ISBN 0-08-024921-3, 1983.

Gordon, R.J. Distribution of airborne polycyclic aromatic hydrocarbons throughout Los Angeles. Environ. Sci. Technol., 10:370-373, 1976.

Gordon, A.G., and E. Gorham. Ecological aspects of air pollution from an iron-sintering plant at Wawa, Ontario. Can. J. Bot., 41:1063-1078, 1963.

Gorham, E. Accumulation of radioactive fallout by plants in the English Lake District. Nature, 181:1523-1524, 1958a.

Gorham, E. Free acid in British soils. Nature, 181:106, 1958b.

Gorham, E. A comparison of lower and higher plants as accumulators of radioactive fallout. Can. J. Bot., 37:327-329, 1959.

Gorham, E. Canada's Peatlands: their importance for the global carbon cycle and possible effects of greenhouse climatic warming. Transactions Royal Soc. Canada. Series V. Vol. 3. 1988a. pp. 21-23.

Gorham, E. Biotic impoverishment of northern peatlands. In: G.M. Woodwell (ed.). Proc. Conference on Biotic Impoverishment. Woods Hole Res. Ctr., 1986. Cambridge Univ. Press, 1988b.

Gorham, E., S.E. Bayley, and D.W. Schindler. Ecological effects of acid deposition upon peatlands: a neglected field in acid-rain research. Can. J. Fish. Aquat. Sci., 41:1256-1268, 1984.

Gorham, E., and N.E. Detenbeck. Sulphate in bog waters: a comparison of ion chromatography with Mackereth's cation exchange technique and a revision of earlier views on causes of bog acidity. J. Ecol., 74:899-903, 1986.

Gorham, E., S.J. Eisenreich, J. Ford, and M.V. Santelmann. The chemistry of bog waters. In: W. Stumm (ed.). Chemical Processes in Lakes. John Wiley and Sons, New York, 1985. pp. 339.

Gorham, E., and A.G. Gordon. Some effects of smelter pollution northeast of Falconbridge, Ontario. Can. J. Bot., 38:307-312, 1960a.

Gorham, E., and A.G. Gordon. The influence of smelter fumes upon the chemical composition of lake waters near Sudbury, Ontario, and upon the surrounding vegetation. Can. J. Bot., 38:477-487, 1960b.

Gorham, E., and A.G. Gordon. Some effects of smelter pollution upon vegetation near Sudbury, Ontario. Can. J. Bot., 41:371-378, 1963.

Gorham, E., and D. Tilton. The mineral content of *Sphagnum fuscum* as affected by human settlement. Can. J. Bot., 56:2755-2759, 1978.

Gorham, E., G.A. Wheeler, J.A. Janssens, and P.H. Glaser. The natural and anthropogenic acidification of peatlands: an overview. In: T.C. Hutchinson and K. Meema (eds.). Effects of Air Pollutants on Forests Agriculture and Wetlands. Springer-Verlag, NY, 1987. pp. 493-512.

Gough, L.P., L.J. Jackson, and J.A. Sacklin. Determining baseline element composition of lichens. II. *Hypogymnia entermorpha* and *Usnea spp.* at Redwood National Park, California. Water, Air, and Soil Pollut., 38:169-180, 1988a.

Gough, L.P., R.C. Severson, and L.L. Jackson. Determining baseline element composition of lichens. I. *Parmelia sulcata* at Theodore Roosevelt National Park, North Dakota. Water, Air, and Soil Pollut., 38:157-167, 1988b.

Gräf, W., and H. Diehl. Concerning the naturally caused normal level of carcinogenic polycyclic aromatics and its cause. Arch. Hyg., 150:49-59, 1966.

Gräf, W., and W. Nowak. Promotion of growth in lower and higher plants by carcinogenic polycyclic aromatics. Arch. Hyg. Bakteriol., 150:513-528, 1966.

Gregor, D.J., and W.D. Gummer. Evidence of atmospheric transport and deposition of organichlorine pesticides and polychlorinated biphenyls in Canadian arctic snow. Environ. Sci. Technol., 23:561-565, 1989.

Grimmer. G. Environmental Carcinogens: Polycyclic Aromatic Hydrocarbons: Chemistry, Occurrence, Biochemistry, Carcinogenicity. CRC Press, Inc., Boca Raton, Florida, 1983. 261 pp.

Grimmer, G., and D. Düvel. Investigations of biosynthetic formation of polycyclic hydrocarbons in higher plants. Z. Naturforsch., 256:1171-1175, 1970.

Groenewegen, D., and H. Stolp. Decomposition of Toxic and Nontoxic Organic Compounds in Soils. Ann Arbor Science, Ann Arbor, Michigan, 1981. pp. 233-240.

Gross, K. P. Vollbrecht, J. Franzen, J. Dietz, and E. Wagner. Untersuchungen zum Mechanismus der neuartigen Waldschaden: Hemmung der Photosynthese und Vergilbung von Fichtenkeimlingen und-Jungpflanzen durch Begasung mit β-Pinen. Allgem. Forst Jagdztg., 159:42-47, 1988.

Grover, R., S.R. Shewchuk, A.J. Cessna, A.E. Smith, and J.H. Hunter. Fate of 2,4-D iso-octyl ester after application to a wheat field. J. Environ. Qual., 14:203-210, 1985.

Gschwend, P.M., and R.A. Hites. Fluxes of polycyclic aromatic hydrocarbons to marine and lacustrine sediments in the northeastern United States. Geochim. Cosmoch. Acta., 45:2359-2367, 1981.

Guderian, R. Air Pollution by Photochemical Oxidants: Formation, Transport, Control, and Effects on Plants. Springer Verlag, New York, 1985. pp. 129-169.

Gudjonsdottir, S., and H. Burstrom. Growth-promoting effects of alcohols on excised wheat roots. Physiol. Plant., 15:498-504, 1962.

Guerin, M. Polycyclic Hydrocarbons and Cancer, 1, Environment, Chemistry and Metabolism. Academic Press, New York, 1978. pp. 3-42.

Gunther, F.A., F. Buzzetti, and W.E. Westlake. Residue Behavior of Polynuclear Hydrocarbons on and in Oranges. Residue Rev., 17:81-104, 1967.

Halliwell, B., and J.M.C. Gutteridge. Oxygen toxicity, oxygen radicals, transition metals, and disease. Biochem. J., 219:1-14, 1984.

Hamilton, S.J., and P.M. Mehrle. Metallothionein in fish: review of its importance in assessing stress from metal contaminants. Trans. Amer. Fish. Soc., 115:596-609, 1986.

Hansch, C., D. Kim, A.J. Leo, E. Novelino, C. Silipo, and A. Vittoria. Toward a quantitative comparative toxicology of organic compounds. CRC Crit. Rev. Toxicol., 19:185-226, 1989.

Hargrave, B.T., W.P. Vass, P.E. Erickson, and B.R. Fowler. Atmospheric transport of organochlorines to the Arctic Ocean. Tellus, 40B:480-493, 1988.

Harley, J.L., and H. Beevers. Acetate utilization by maize roots. Plant Physiol., 38:117-123, 1963.

Harms, H. Metabolism of benzo[a]pyrene in plant cell cultures and wheat seedlings. Landbauforsch. Voelkenrode, 25:83-90, 1975.

Harper, D.B., and R.L. Wain. Studies on plant growth-regulating substances. XXX. The plant growth-regulating activity of substituted phenols. Ann. Appl. Biol., 64:395-407, 1969.

Harris, C.R., and W.W. Sans. Absorption of organochlorine insecticide residues from agricultural soils by root crops. J. Agric. Food Chem., 15:861-863, 1967.

Harrison, F., K. Watness, D. Nelson, J. Miller, and A. Calabrese. Mercury-binding proteins in the slipper limpet, *Credipdula fornicata*, exposed to increased soluble mercury. Estuaries, 10:78-83, 1987.

Hay, J.R. Herbicide transport in plants. In: L.J. Audus (ed.). Herbicides: Physiology, Biochemistry, Ecology. Vol.1. Academic Press, London, 1976. pp. 365-396.

Heit, M., C. Klusek, and J. Baron. Evidence of deposition of anthropogenic pollutants in remote Rocky Mountain lakes. Water, Air, and Soil Pollut., 22:403-416, 1984.

Heit, M., Y. Tan, C. Klusek, and J.C. Burke. Anthropogenic trace elements and polycyclic aromatic hydrocarbon levels in sediment cores from two lakes in the Adirondack acid lake region. Water, Air, and Soil Pollut., 15:441-464, 1981.

Heit, M., Y.L. Tan, and K.M. Miller. The origin and deposition history of polycyclic aromatic hydrocarbons in the Finger Lakes Region of New York. Water, Air, and Soil Pollut., 37:85-110, 1988.

Helmer, E.H., N.R. Urban, and S.J. Eisenreich. Aluminum geochemistry in peatland waters. Biogeochem., 9:247-276, 1990.

Hemond, H.F. Biogeochemistry of Thoreau's Bog, Concord. Mass. Ecol. Monogr., 50:507-526, 1980.

Hemond, H.F. The nitrogen budget of Thoreau's Bog. Ecology, 64:99-109, 1983.

Henderson, A. Literature on air pollution and lichens XXVII. Lichenologist, 19:433-437, 1988.

Hicks, B.B. Measuring dry deposition: A re-assessment of the state of the art. Water, Air, Soil Pollution, 30:75-90, 1986.

Hilton, H.W., N.S. Nomura, S.S.Kameda, and W.L. Yauger. Some patterns of herbicide and growth regulator intake, persistence, and distribution in sugarcane. Arch. Environ. Contam. Toxicol., 4:385-394, 1976.

Hinckley, D.A., and T.F. Bidleman. Analysis of pesticides in seawater after enrichment onto C_8 bonded-phase cartridges. Environ. Sci. Technol., 23:995-1000, 1989.

Hinkel, M., A. Reischl, K.-W. Schramm, F. Trautner, M. Reissinger, and O. Hutzinger. Concentration levels of nitrated phenols in conifer needles. Chemosphere, 18:2433-2439, 1989.

Hoff, R.M., and K.W. Chan. Atmospheric concentrations of chlordane at Mould Bay, N.W.T., Canada. Chemosphere, 14:449-452, 1986.

Horne, R.A. Marine Chemistry. John Wiley and Sons, Inc., 1969, pp. 140.

Houghton, R.A. Estimating changes in the carbon content of terrestrial ecosystems from historical data. In: J.R. Trabalka and Riechle, D.R. (eds.). The Changing Carbon Cycle. Springer, NY, 1986. pp. 175-193.

Howe, J. Runoff of Agrichemicals into a Nontidal Estuary. M.S. Thesis. Univ. of Minnesota, Minneapolis, MN, 1990.

Huckins, J.N., J.D. Petty, and D.C. England. Distribution and impact of trifluralin, atrazine and fonofos residues in microcosms simulating a northern prairie wetland. Chemosphere, 15:563-588, 1986.

Hurwitz, B., E.J. Pell, and R.T. Sherwood. Status of coumestrol and 4,7-dihydroxyflavone in alfalfa foliage exposed to ozone. Phytopath., 69:810-813, 1979.

Hutchinson, T.C., L. Bozic, and G. Munoz-Vega. Responses of five species of conifer seedlings to aluminum stress. Water, Air, and Soil Pollut., 31:283-294, 1986.

Igawa, M., J.W. Munger, and M.R. Hoffmann. Analysis of aldehydes in cloud- and fogwater samples by HPLC with a postcolumn reaction detector. Environ. Sci. Technol., 23:556-561, 1989.

Imbamba, S.K., and D.N. Moss. Effect of atrazine on physiological processes in leaves. Crop Sci., 11:844-848, 1971.

Isensee, A.R., and G.E. Jones. Absorption and translocation of root and foliage applied 2,4-dichlorophenol, 2,7-dichlorodibenzo-p-dioxin, and 2,3,7,8-tetrachlordibenzo-p-dioxin. J. Agric. Food Chem., 19:1210-1214, 1971.

Iwata, Y., and F.A. Gunther. Translocation of the polychlorinated biphenyl Aroclor 1254 from soil into carrots under field conditions. Arch. Environ. Contam. Toxicol., 4:44-59, 1976.

Jackson, D.R., and A.P. Watson. Disruption of nutrient pools and transport of heavy metals in a forested watershed near a lead smelter. J. Environ. Qual., 6:331, 1977.

James, P.W. The Effect of Air Pollutants Other Than Hydrogen Fluoride and Sulphur Dioxide on Lichens. In: B.W. Ferry, M.S. Baddeley and D.L. Hawksworth (eds.). Air Pollution and Lichens, . The Athlone Press, London, 1973. pp. 143-175.

Jarvis, B.W., G.E. Lange, and R.K. Wieder. Arylsulphatase activity in peat exposed to acid precipitation. Soil Biol. Biochem., 19:107-109, 1987.

Jimenez, B.D., L.S. Burtis, G.H. Ezell, B.Z. Egan, N.E. Lee, J.J. Beauchamp, and J.F. McCarthy. Mixed function oxidase system of bluegill sunfish *Lepomis macrochirus*: correlation of activities in feral and experimental fish. Environ. Toxicol. Chem., 7:623-634, 1988.

Johnson, A.R. Diagnostic variables as predictors of ecological risk. Environ. Manage., 12:515-523, 1988.

Johnson, A.H., T.G. Siccama, and A.J. Friedland. Spatial and temporal patterns of lead accumulation in the forest floor in the northeastern United States. J. Environ. Qual., 11:588, 1982.

Jones, K.C., J.A. Stratford, K. S. Waterhouse, E. T. Furlong, W. Giger, R.A. Hites, C. Schaffner, and A.E. Johnston. Increases in the polynuclear aromatic hydrocarbon content of an agricultural soil over the last century. Environ. Sci. Technol., 23:95-101, 1989.

Jones, D., M.J. Wilson, and J.R. Laundon. Observations on the location and form of lead in *Stereocaulon vesuvianum*. Lichenologist, 14:281, 1982.

Kanter, P.M., and H.S. Schwartz. A fluorescence enhancement assay for cellular DNA damage. Molec. Pharmacol., 22:145-151, 1982.

Kaplan, D.I., W.G. Burkman, and D.C. Adriano. Response of loblolly pine (*Pinus taeda* L.) to soil-applied organo-borates. Water, Air, and Soil Pollut., 37:73-83, 1988.

Kappus, H. Oxidative stress in chemical toxicity. Arch. Toxicol., 60:144-149, 1987.

Karin, M. Metallothioneins: Proteins in search of function. Cell, 41:9-10, 1985.

Karns, D.R. Toxic Bog Water in northern Minnesota Peatlands: Ecological and Evolutionary consequences for Breeding Amphibians. Ph.D. Thesis. University of Minnesota, MN, 1984. 164 pp.

Katz, M., C. Chan, H. Tosine, and T. Sakuma. Polynuclear Aromatic Hydrocarbons: Third International Symposium on Chemistry and Biology--Carcinogenels and Mutageneis. Ann Arbor Science, Ann Arbor, Michigan, 1979. pp. 171-189.

Kaufman, D.D. Phenols. In: P.C. Kearney and D.D. Kaufman (eds.). Herbicides: Chemistry, Degradation, and Mode of Action, 2nd edition. Marcel Dekker, New York, 1976. pp. 665-707.

Kaushik, C.P., M.K.K. Pillai, A. Raman, and H.C. Agarwal. Organochlorine insecticide residues in air in Delphi, India. Water, Air, and Soil Pollut., 32:63-76, 1987.

Kawano, M., T. Inoue, T. Wada, H. Hidake, and R. Tatsukawa. Bioconcentration and residue patterns of chlordane compounds in marine animals: invertebrates, fish, mammals, and seabirds. Environ. Sci. Technol., 22:792-797, 1988.

Keen, N.T., and O.C. Taylor. Ozone injury in soybeans: Isoflavinoid accumulation is related to necrosis. Plant Physiol., 55:731-733, 1975.

Keizer, P.D., D.C. Gordon, and J. Dale. Hydrocarbons in eastern Canadian marine waters determined by fluorescence spectroscopy and gas-liquid chromatography. J. Fish. Res. Board Can., 34:347-353, 1977.

Kelly, J.R., and M.A. Harwell. Comparisons of the processing of elements by ecosystems: I. Nutrients. Ecosys. Res. Ctr. Report No. 21. Cornell University, 1982.

Khan, A.A., and S.S. Malhotra. Effects of aqueous sulphur dioxide on pine needle glycolipids. Phytochem., 16:539-543, 1977.

Kilzer, L., I. Scheunert, H. Geyer, W.Klein, and F. Korte. Laboratory screening of the volatilization rates of organic chemicals from water and soil. Chemosphere, 10:751-761, 1979.

Kimmerer, T.W., and T.T. Kozlowski. Ethylene and ethane, acetaldehyde and ethanol production by plants under stress. Plant Physiol., 69:840-847, 1982.

Kirkwood, R.C. Action on respiration and intermediary metabolism. In: L.J. Audus (ed.). Herbicides: Physiology, Biochemistry, Ecology. Vol. 1. Academic Press, London, 1976. pp. 444-492.

Kivinen, E., and P. Pakarinen. Peatland areas and the proportion of virgin peatlands in different countries. Proc. 6th Int. Peat Congr., Duluth, 1981. pp. 52-54.

Klepper, L.A. Effects of certain herbicides and their combinations on nitrate and nitrite reduction. Plant Physiol., 64:273-275, 1979.

Klingler, H., and E. Wagner. Pleiotropic *in vitro* effects of β-pinene on plant membrane microsomes separated by free-flow-electrophoresis. In International Congress on Forest Decline Research: State of Knowledge and Perspectives. Forschungsbeirat Waldschaden/Luftverunreinigungen der Bundesregierung und der Lander, Lake Constance, West Germany, 1989. pp. 307.

Kochhar, T.S., P.R. Bhalla, and P.S. Sabharwal. *In vitro* induction of vegetative buds by benz[a]anthracene in tobacco callus. Planta, 94:246-249, 1970.

Koerselman, W., H. De Caluwe, and W.M. Kieskamp. Denitrification and dinitrogen fixation in two quaking fens in the Vechtplassen area, The Netherlands. Biogeochem., 8:153-166, 1989.

Kojima, Y., and J. Kagi. Metallothionein. Trends in Biochem. Sci., 3:90-93, 1978.

Kolar, L., R. Ledvina, J. Ticha, and F. Hanus. Contamination of soil, agricultural crops, and vegetables by 3,4-benzpyrene in the vicinity of Ceske Budejovice. Cesk. Hyg., 20:135-139, 1975.

Korfmacher, W.A., E.L. Wehry, G. Mamantov, and D.F.S. Natusch. Resistance to photochemical decomposition of polycyclic aromatic hydrocarbons vapor-adsorbed on coal fly ash. Science, 207:763-765, 1980.

Korner, C., J.S. Scheel, and H. Bauer. Maximum leaf diffusive conductance in vascular plants. Photosynthetica, 13:45-82, 1979.

Koziol, M.J., and F.R. Whatley. Gaseous Air Pollutants and Plant Metabolism. Butterworths, London. ISBN 0-408-11152-6, 1984.

Kreuzig, R., I. Bebefugi, M. Bahadir, and F. Korte. Jahresverlauf der Luftkonzentrationen anthropogener und biogener Kohlenwasserstoffe an drei unterschiedlich belasteten bayerischen Waldstandorten. Zentralbl. gesamte Forstwesen, 105:125-132, 1988.

Krstich, M.A., and O.J. Schwarz. Characterization of ^{14}C-napthol uptake in excised root segments of clover (*Trifolium pratense* L.) and fescue (*Festuca arundinaceae* Screb.). Environmental Monitoring and Assessment, 13:35-44, 1989.

Kuchler, A.W. Potential Natural Vegetation of the Conterminous United States. American Geographical Society Pub. 36. Princeton Polychrome Press, 1964.

Kuster, H., R. Kaa, and K.E. Rehfuess. Beziehungen zwischen der Landnutzung und der Deposition von Blei und Cadmium in Torfen am Nordrand der Alpen. Naturwiss., 75:611-613, 1988.

Kveseth, K., B. Sortland, and M. Stobet. Polycyclic Aromatic Hydrocarbons in Leafy Vegetables: A Comparison of the Nordic Results. Nordic PAH-Project. Report No. 8. Central Institute for Industrial Research, Oslo, Norway, 1981. 10 pp.

Lantzy, R.J., and F.T. Mackenzie. Atmospheric trace metals: global cycles and assessment of man's impact. Geochem. et Cosmochem. Acta., 43:511, 1979.

Larson, D.W. Water Relations, and Lichens. In: Progress and Problems in Lichenology in the Eighties, E. Peveling, ed. Cramer: Berlin and Stuttgart, 1987. pp. 351-360.

Larson, R.A., and M.R. Berenbaum. Environmental phototoxicity. Environ. Sci. Technol., 22:354-360, 1988.

LeBlanc, F., D.N. Rao, and G. Comeau. The epiphytic vegetation of *Populus balsamifera* and its significance as an air pollution indicator in Sudbury, Ontario. Can. J. Bot., 50:519-528, 1972.

Lech, J.J., M.J. Vodicnik, and C.R. Elcombe. Induction of monooxygenase activity in fish. In: J. Lavern and J. Weber (ed.). Aquatic Toxicology. Raven Pess, New York, 1982. pp. 1:107-148.

Lee, J.A., M.C. Press, S. Woodin, and P. Ferguson. Responses to acidic deposition in ombrotrophic mires. In: T.C. Hutchinson and K.M. Meema (eds.). Effects of Air Pollutants on Forests, Agriculture and Wetlands. Springer-Verlag, NY, 1987. pp. 549-560.

Lee, J.A., and J.H. Tallis. Regional and historical aspects of lead pollution in Britain. Nature, 245:216-218, 1973.

Lefohn, A.S., and V.C. Runeckles. Establishing standards to protect vegetation - ozone exposure/dose considerations. Atmos. Environ., 21:561-568, 1987.

Leuenberger, C., J. Czuczwa, J. Tremp, and W. Giger. Nitrated phenols in rain: atmospheric occurrence of phytotoxic pollutants. Chemosphere, 17:511-515, 1988.

Levin, W.A., W. Wood, P.G. Wislocki, R.L. Chang, J. Kapitulnik, H.D. Mah, H. Yagi, D.M. Jerina, and A.H. Cooney. Polycyclic Hydrocarbons and Cancer: Environment, Chemistry, and Metabolism. Academic Press, New York, 1978. pp. 189-202.

Lichtenstein, E.P., T.W. Fuhremann, N.E.A. Scopes, and R.F. Skrentny. Translocation of insecticides from soils into pea plants: effects of the detergen LAS on translocation and plant growth. J. Agric. Food Chem., 15:864-869, 1967.

Lichtenstein, E.P., and K.R. Schulz. Residues of aldrin and heptachlor in soils and their translocation into various crops. J. Agric. Food Chem., 13:57-63, 1965.

Ligocki, M.P., and J.F. Pankow. Measurements of the gas/particle distributions of atmospheric organic compounds. Environ. Sci. Technol., 23:75-83, 1989.

Linck, A.J. Effects on the cytology and fine structure of plant cells. In: L.J. Audus (ed.). Herbicides: Physiology, Biochemistry, Ecology. Academic Press, New York, 1976. pp. 83-125.

Lindberg, S. E. Emission and Deposition of Atmospheric Mercury Vapor. In: Lead, Mercury, Cadmium and Arsenic in the Environment. T.C. Hutchinson and K.M. Meema (eds.). John Wiley and Sons, New York, Chapter 8, 1987.

Linne, C., and R. Martens. Examination of the risk of contamination by polycyclic aromatic hydrocarbons in the harvested crops of carrots and fungi after the application of composted municipal waste. Z. Pflanzenernaehr. Bodenkd., 141:265-274, 1978.

Livett, E.A., J.A. Lee, and J.H. Tallis. Lead, zinc, and copper analyses of British blanket peats. J. Ecol., 67:865-891, 1979.

Loar, J.M., S.M. Adams, B.G. Blaylock, H.L. Boston, M.A. Huston, B.L. Kimmel, J.T. Kitchens, C.R. Olson, M.G. Ryon, J.G. Smith, G.R. Southworth, A.J. Stewart, B.T. Walton, H. Amano, C.T. Garten, and L.J. Meyers. First Annual Report on the ORNL Biological Monitoring and Abatement Program. ORNL/TM-10399, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1987a.

Loar, J.M., S.M. Adams, H.L. Boston, B.D. Jimenez, J.F. McCarthy, J.G. Smith, G.R. Southworth, and A.J. Stewart. First Annual Report on the Y-12 Plant Biological Monitoring and Abatement Program. ORNL/TM-10399, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1987b.

Lodenius, M. Regional distribution of mercury in *Hypogymnia physodes* in Finland. Ambio., 10:183-184, 1981.

Lodenius, M., A. Seppanen, and A. Uusi-Rauva. Sorption and mobilization of mercury in peat soil. Chemosphere, 12:1575-1581, 1983.

Lodenius, M., A. Seppanen, and S. Autio. Leaching of Hg from peat soil. Chemosphere, 16:1215-1220, 1987.

Looney, J.H.H., and P.W. James. In: M. Ashmore, N. Bell, and C. Garretty (eds.). Acid Rain and Britain's Natural Ecosystems. Imperial College, London, 1988. pp. 13-25

Lovett, G.M. Rates and mechanisms of cloud water deposition to a subalpine balsam fir forest. Atmos. Environ., 18:361-371, 1984.

Lovett, G.M., S.E. Lindberg, D.D. Richter, and D.W. Johnson. The effects of acidic deposition on cation leaching from three deciduous forest canopies. Can. J. For. Res., 15:1055, 1985.

Lovett, G.M., W.A. Reiners, and R.K. Olson. Cloud droplet deposition in subalpine balsam fir forests: hydrological and chemical inputs. Science, 218:1303, 1982.

Lu, A.Y., and S.B. West. Multiplicity of mammalian microsomal cytochromes P-450. Pharmacol. Rev., 31:277-295, 1980.

Lunde, G., and A. Bjorseth. Polycyclic aromatic hydrocarbons in long-range transported aerosols. Nature, 268:518-519, 1977.

Lurmann, F.W., A. Lloyd, and B. Nitta. Modeling potential ozone impacts from natural hydrocarbons. II. Hypothetical biogenic HC emission scenario modeling. Atmos. Environ., 17:1951-1963, 1983.

Lyall, R.J., M.A. Hooper, and S.J. Mainwaring. Polycyclic aromatic hydrocarbons in the Latrobe Valley. Atmos. Environ., 22:2549-2555, 1988.

Mackay, D., S. Paterson, and W.H. Schroeder. Model describing the rates of transfer processes of organic chemicals between atmosphere and water. Environ. Sci. Technol., 20:810-816, 1986.

Mackay, D., W.Y. Shiu, and R.P. Sutherland. Determination of air-water Henry's Law constants for hydrophobic pollutants. Environ. Sci. Technol., 13(3):333-337, 1979.

MacKenzie, J.J., and M.T. El-Ashry. Air Pollution's Toll on Forests and Crops. Yale University Press, New Haven, 1989. pp. 1-21.

Majumdar, S.K., and R. S. Newton. Morphogenic and cytogenetic effects of 7,12-dmethylbenz[a]anthracene on *Haworthia* callus *in vitro*. Experientia, 28:1497-1498, 1972.

Malhotra, S.S., and A.A. Khan. Biochemical and physiological impact of major pollutants. In: M. Treshow (ed.). Air Pollution and Plant Life. John Wiley & Sons Ltd. New York. ISBN 0-471-90103-2, 1984.

Malhotra, S.S., and A.A. Khan. Effects of sulphur dioxide fumigation on lipid biosynthesis in pine needles. Phytochem., 17:241-244, 1978.

Malone, C.R. Effects of a nonselective arsenical herbicide on plant biomass and community structure in a fescue meadow. Ecology, 53:507, 1972.

Marrs, R.H. The effects of potential bracken and scrub control herbicides on lowland *Calluna* and grass heath communities in East Anglia, UK. Biol. Conserv., 32:13, 1985.

Marrs, R.H., C.T. Williams, A.J. Frost, and R.A. Plant. Assessment of the effects of herbicide spray drift on a range of plant species of conservation interest. Environ. Pollut., 59:71, 1989.

Martineau, D., A. Lagace, P. Beland, R. Higgins, D. Armstrong, and L.R. Shugart. Pathology of stranded beluga whales (*Delphinapterus leucas*) from the St. Lawrence estuary, Quebec, Canada. J. Comp. Pathol., 98:287-311, 1988.

Mason, R.P., and C.F. Chignell. Free radicals in pharmacology and toxicology--selected topics. Pharacol. Rev., 33:189-211, 1982.

Masterson, W.L., and T.P. Lee. Effect of dissolved salts on water solubility of lindane. Environ. Sci. Technol., 6(10):919-921, 1972.

Mather-Minaich, E., and R.T. DiGiulio. Antioxidant enzyme activities and malondialdehyde, glutathione and methemoglobin concentration in channel catfish exposed to DEF and N-butyl mercaptan. Comp. Biochem. Physiol., 85:427-432, 1986.

Matthews, E., and I. Fung. Methane emission from natural wetlands: Global distribution, area and environmental characteristics of sources. Global Biogeochem. Cycles, 1:61-86, 1987.

Mattson, S., and E. Koutler-Andersson. Geochemistry of a raised bog: some nitrogen relationships. Kungl. Lantbrukshoegsk. Annaler., 22:221-224, 1955.

Matzner, E. Annual rates of deposition of polycyclic aromatic hydrocarbons in different forest ecosystems. Water, Air, and Soil Pollut., 21:425-434, 1984.

Mayer, A.M., and M. Evenari. The activity of organic acids as germination inhibitors and its relation to pH. J. Exp. Bot., 4:257-263, 1953.

McBee, K., and J.W. Bickham. Petrochemical related DNA damage in wild rodents detected by flow cytometry. Bull. Environ. Contam. Toxicol., 40:343-349, 1988.

McCarthy, J.F., B.D. Jimenez, L.R. Shugart, F.V. Sloop, and A. Oikari. Biological markers in animal sentinels: Laboratory studies improve interpretation of field data. In: S. Sandhu (ed.), In situ. Evaluation of Biological Hazards. Plenum Press, New York. 1989.

McClure, V.E., and J. Lagrange. Deposition of heavy chlorinated hydrocarbons from the atmosphere. Bull. Environ. Contam. Toxicol., 17:219-224, 1977.

McCrady, J.K., C. McFarlane, and F.T. Lindstrom. The transport and affinity of substituted benzenes in soybean stems. J. Exp. Bot., 38:1875-1890, 1987.

McCrea, R.C., and J.D. Fischer. Heavy metal and organochlorine contaminants in the five major Ontario rivers of the Hudson Bay Lowland. Water Pollut. Res. J. Can., 21:225-234, 1986.

McCrea, R.C., and G.M. Wickware. Organochlorine contaminants in peatlands and selected estuary sites of the Moose River. Water Pollut. Res. J. Can., 21:251-256, 1986.

McFarlane, C. The uptake, distribution and metabolism of four organic chemicals by soybean plants and barley roots. Environ. Toxicol. Chem., 6:847-856, 1987.

McFarlane, C., C. Nolt, C. Wickliff, T. Pfleeger, R. Shimbuku, and M. McDowell. The uptake, distribution and metabolism of four organic chemicals by soybean plants and barley roots. Environ. Toxicol. Chem., 6:847-856, 1987a.

McFarlane, C., T. Pfleeger, and J. Fletcher. Transpiration effect on the uptake and distribution of bromacil, nitrobenzene, and phenol in soybean plants. J. Environ. Qual., 16:372-376, 1987b.

McFarlane, C., T. Pfleeger, and J. Fletcher. Effect, uptake and disposition of nitrobenzene in several terrestrial plants. Environ. Toxicol. Chem., 9:513-520, 1990.

McFarlane, C., and C. Wickliff. Excised barley root uptake of several ^{14}C labeled organic compounds. Environmental Monitoring and Assessment, 5:385-391, 1985.

Mehlhorn, H., Francis, B.J., and A.R. Wellburn. Prediction of the probability of forest decline damage to Norway spruce using three simple site-independent diagnostic parameters. New Phytol., 110:525-534, 1988.

Menn, J.J., and G.G. Still. Metabolism of insecticides and herbicides in higher plants. CRC Crit. Rev. Toxicol., 5:1-22, 1977.

Meredith, M.L., and R.A. Hites. Polychlorinated biphenyls in tree bark and wood growth rings. Environ. Sci. Technol., 21:709-712, 1987.

Metcalf, R.L. Organic Insecticides: Their Chemistry and Mode of Action. Interscience Pub., New York, 1955. pp. 214.

Miller, W.P., and W.W. McFee. Distribution of cadmium, zinc, copper, and lead in soils of industrial northwestern Indiana. J. Environ. Qual., 12:29, 1983.

Miller, W.P., W.W. McFee, and J.M. Kelly. Mobility and retention of heavy metals in sandy soils. J. Environ. Qual., 12:579, 1983.

Mitane, Y., C. Tohyama, and H. Saito. The role of metallothionein in the elevated excretion of copper in urine of people living is a cadmium-polluted area. Fundam. Appl. Toxicol., 6:285-291, 1986.

Moreland, D.E., and J.L. Hilton. Actions on photosynthetic systems. In: L.J. Audus (ed.). Herbicides: Physiology, Biochemistry, Ecology. Vol. 1. Academic Press, London, 1976. pp. 493-524.

Morgan, P.W. Effects on ethylene physiology. In: L.J. Audus (ed.). Herbicides: Physiology, Biochemistry, Ecology. Vol.1. Academic Press, London, 1976. pp. 255-280.

Morrod, R.S. Effects on plant cell membrane structure and function. In: L.J. Audus (ed.). Herbicides: Physiology, Biochemistry, Ecology. Vol. 1. Academic Press, London, 1976. pp. 281-304.

Mount, D.R., J.R. Hockett, and W.A. Gern. Effect of long term exposure to acid, aluminum, and low calcium on adult brook trout (*Salvelinus fontinalis*): Vitellogenesis and osmoregulation. Can. J. Fish. Aquat. Sci., 45:1633-1642, 1988.

Moza, P.N., I. Scheunert, and F. Korte. Fate of chloroalkylene-9-^{14}C in carrots, sugar beets, and soil under outdoor conditions. Arch. Environ. Contam. Toxicol., 8:183-189, 1979.

Mrozek, E., Jr., and R.B. Leidy. Investigation of selective uptake of polychlorinated biphenyls by *Spartina alterniflora* Loisel. Bull. Environ. Contam. Toxicol., 27:481-488, 1981.

Mudd, J.B. Peroxyacyl nitrates. In: J.B. Mudd and T.T. Kozlowski (eds.). Responses of Plants to Air Pollution. Academic Press, New York, 1975. pp. 97-121.

Mudd, J.B., McManus, T.T., and A. Ongun. Inhibition of lipid metabolism in chloroplasts by ozone. In: H.H. England and W.T. Beery (eds.). Proc. 2nd Int. Clean Air Congr., 1970. Academic Press. New York, 1971a.

Mudd, J.B., McManus, T.T., Ongun, A., and T.E. McCollogh. Inhibition of glycolipid biosynthesis in chloroplasts by ozone and sulphydryl reagent. Plant Physiol., 48:335-339, 1971b.

Mueller, C.S., R.L. Thompson, G.J. Ramelow, J.N. Beck, M.P. Langley, J.C. Yound, and D.M. Casserly. Distribution of Al, V, and Mn in lichens across Calcasieu Parish, Louisiana. Water, Air, and Soil Pollut., 33:155-164, 1986.

Muir, D.C.G. Phosphate esters. In: O. Hutzinger (ed.). The Handbook of Environmental Chemistry: Anthropogenic Compounds, Volume 3, Part C. Springer-Verlag, New York, 1984. pp. 41-66.

Muir, D.C.G., N.P. Grift, C.A. Ford, Q.W. Reiger, M.R. Hendzel, and W.L. Lockhart. Evidence for Long-Range Transport of Toxaphene to Remote Arctic and Subarctic Waters from Monitoring of Fish Tissue. In: D.A. Kurtz (ed.). Long-Range Transport of Pesticides. Lewis Publishers, Chelsea, MI, 1990.

Muir, D.C., R.J. Norstrom, and M. Simon. Organochlorine contaminants in arctic marine food chains: accumulation of specific polychlorinated biphenyls and chlordane-related compounds. Environ. Sci. Technol., 22:1071-1085, 1988.

Mulawa, P.A., S.H. Cadle, F. Lipari, C.C. Ang, and R.T. Vandervennet. Urban dew: its composition and influence on dry deposition rates. Atmos. Environ., 20:1389-1396, 1986.

Mullen, P.W. Toxicology of acid rain. Environ. Sci. Technol., 20:211, 1986.

Müller, V.H. Uptake of 3,4-Benzopyrene by Food Plants from Artificially Enriched Substrates. Z. Pflanzenernaehr. Bodenkd., 6:685-695, 1976.

Munger, J.W., J. Collett, Jr., B.C. Daube, Jr., and M.R. Hoffman. Carboxylic acids and carbonyl compounds in southern California clouds and fogs. Tellus, 41B:230-242, 1989.

Murozumi, M., T.J. Chow, and C.C. Patterson. Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata. Geochim. Mosmochim. Acta.,33:1247-1294, 1969.

Murphy, T.J. Atmospheric inputs of chlorinated hydrocarbons to the Great Lakes. In: J.O. Nriagu and M.S. Simmons (eds.). Toxic Contaminants in the Great Lakes. John Wiley & Sons, New York, 1984. pp. 53-79.

Muzik, T.J. Influence of environmental factors on toxicity to plants. In: L.J. Audus (ed.). Herbicides: Physiology, Biochemistry, Ecology. Vol. 2. Academic Press, London, 1976. pp. 204-248.

Nakamura, H., and H. Saka. Photochemical oxidants injury in rice plants. III. Effect of ozone on physiological activities in rice plants. Jap. J. Crop Sci., 47:707-714, 1978.

Nash, R.G., and L.M. Beall. Chlorinated hydrocarbon insecticides: root uptake vs. vapor contamination of soybean foliage. Science, 168:1109-1111, 1970.

Nash, R.G., M.G. Beall, Jr., and E.A. Woolson. Plant uptake of chlorinated insecticides from soils. Agron. J., 62:369-372, 1970.

Nash III, T.H. Simplification of the Blue Mountain lichen communities near a zinc factory. Bryologist, 75:315-324, 1972.

Nash III, T.H. Influence of effluents from a zinc factory on lichens. Ecol. Mongr., 45:183-198, 1975.

Nash III, T.H. Tolerance to Heavy Metals. In: J. Shaw (ed.). Metal Tolerance in Plants: Evolutionary Aspects. CRC Press: Boca Raton, Florida, 1989. pp. 119-131.

Nash III, T.H., and M.R. Sommerfeld. Elemental concentrations in lichens in the area of the Four Corners Power Plant, New Mexico. Environ. Exp. Bot., 21:153-162, 1981.

Nash III, T.H., and V. Wirth. Lichens, Bryophytes and Air Quality. Cramer: Berlin and Stuttgart, 1988.

National Academy of Science (NAS). Particulate Polycyclic Organic Matter, Washington, DC, 1972.

National Research Council. Committee on biological markers. Environ. Health Perspect., 74:3-9, 1987.

Naylor, A.W. Herbicide metabolism in plants. In: L.J. Audus (ed.). Herbicides: Physiology, Biochemistry, Ecology. Vol.1. Academic Press, London, 1976. pp. 397-426.

Ng, A., and C.C. Patterson. Natural concentrations of lead in ancient Arctic and Antarctic ice. Geochim. Cosmochim. Acta., 45:2109-2121, 1981.

Nicholson, K.W. A review of particle resuspension. Atmos. Environ., 22:2639-2651, 1988.

Nieboer, E., D.H.S. Richardson, and F.D. Tomassini. Mineral uptake and release by lichens: an overview. Bryologist, 81:226-246, 1978.

Nieboer, E., and D.H.S. Richardson. The replacement of the nondescript term "Heavy Metal" by a biologically and chemically significant classification of metal ions. Environ. Pollut., 1:3-26, 1980.

Nieboer, E., and D.H.S. Richardson. Lichens as monitors of atmospheric deposition. In: Atmospheric Pollutants in Natural Waters, S.J. Eisenreich, ed. Ann Arbor Science: Ann Arbor, 1981. pp. 339-388.

Nieboer, E., D.H.S. Richardson, L.J.R. Boileay, B.J. Beckett, P. Lavoie, and D. Padovan. Lichens and mosses as monitors of industrial activity associated with uranium mining in northern Ontario, Canada. 3: Accumulations of iron and titanium and their mutual dependence. Environ. Pollut., 4:181-192, 1982.

Noeske, O., A. Lauchli, O.L. Lange, G.H. Vieweg, and H. Ziegler. Konzentration und Lokalisierung von Schwermetallen in Flechten der Erzschlackenhalden des Harzes. Dtsch. Bot. Ges., 4:67-79, 1970.

Nojima, K., and S. Kanno. Studies on photochemistry of aromatic hydrocarbons. IV. Mechanism of formation of nitrophenols by the photochemical reaction of benzene and toluene with nitrogen oxides in air. Chemosphere, 6:371-376, 1977.

Norby, R.J. Foliar nitrate reductase: a marker for assimilation of nitrogen oxides. In: Proceedings of the Workshop on Markers of Air Pollution Effects in Forests. April 25-27, 1988. Little Switzerland, North Carolina. National Research Council, Washington, DC, 1989.

Norstrom, R.J., and D.C.G. Muir. Proceedings 2nd World Conference on Large Lakes. Lewis Pub., Chelsea, MI, pp. 83-112, 1988.

Norstrom, R.J., M. Simon, D.C.G. Muir, and R.E. Schweinsburg. Organochlorine contaminants in arctic marine food chains: identification, geographical distribution, and temporal trends in polar bears. Environ. Sci. Technol., 22(9):1063-1071, 1988.

Norton, S.A. Geochemistry of Maine peat bogs. Maine Geol. Survey, 1983. 62 pp.

Norton, S.A., and J.S. Kahl. A comparison of lake sediments and ombrotrophic peat deposits as long-term monitors of atmospheric pollution. In: T.P. Boyle (ed.). New Approaches to Monitoring Aquatic Ecosystems, ASTM, Philadelphia, 1987. pp. 40-57.

Nriagu, J.O. The Global Cycle of Mercury. In: The Biogeochemistry of Mercury in the Environment. J.O. Nriagu (ed.). Elsevier, Chapter 1, 1979a.

Nriagu, J.O. The Global Copper Cycle. In: J.O. Nriagu (ed.). Copper in the Environment. John Wiley and Sons, Chapter 1, 1979b.

Nriagu, J.O. Global Cadmium Cycle. In: J.O. Nriagu (ed.). Cadmium in the Environment. John Wiley and Sons, Chapter 1, 1980a.

Nriagu, J.O. The Global Nickel Cycle. In: J.O. Nriagu (ed.). Nickel in the Environment. John Wiley and Sons, Chapter 1, 1980b.

Nriagu, J.O., D.A. Holdway, and R.D. Coker. Biogenic sulfur and the acidity of rainfall in remote areas of Canada. Science, 237:1189-1192, 1987.

Nriagu, J.O., and M.S. Simmons (eds.). Toxic Contaminants in the Great Lakes. John Wiley & Sons, New York. 1984.

Nygard, S., and L. Harju. A study of the short range pollution around a power plant using heavy fuel oil by analysing vanadium in lichens. Lichenologist, 15:89-93, 1983.

O'Connor, G.A., D. Kiehl, G.A. Eiceman, and J.A. Ryan. Plant uptake of sludge-borne PCBs. J. Environ. Qual., 19:113-118, 1990.

Ochiai, E. Bioinorganic Chemistry: An Introduction. Allyn and Bacon, Boston, 1977.

Oehme, M., and B. Ottar. The long range transport of polychlorinated hydrocarbons to the Arctic. Geophys. Res. Letters, 11:1133-1136, 1984.

Oehme, M., and H. Stray. Quantitative determination of ultratraces of chlorinated compounds in high-volume air samples from the Arctic using polyurethane foam as collection medium. Fresenius Z. Anal. Chem., 311:665-673, 1982.

Oertli, J.J., and N. Ahmadi. The effect of Systox on ionic fluxes in excised barley roots. Arch. Environ. Contam. Toxicol., 3:97-114, 1975.

Oldfield, F., R. Thompson, and K. Barber. Changing atmospheric fallout of magnetic particles recorded in recent ombrotrophic peat sections. Science, 199:679-680, 1978.

Oldfield, F., K. Tolonen, and R. Thompson. Magnetic measurements of particulate atmospheric pollution history in dated Finnish peat profiles. Ambio, 10:185-188, 1980.

Olmez, I., M.C. Gulovali, and G.E. Gordon. Trace element concentrations in lichens near a coal-fired power plant. Atmos. Environ., 19:1663-1670, 1985.

Ormrod, D.P. Air pollutant interactions in mixtures. In: M.H. Unsworth and D.P. Ormrod (eds.). Effects of Gaseous Air Pollution in Agriculture and Horticulture. Butterworth's, London, 1982. pp 307-331.

Osterman-Golkar, S., L. Ehrenberg, D. Segerback, and I. Halstrom. Evaluation of genetic risks of alkylating agents. II. Hemoglobin as a dose monitor. Mutat. Res., 34:1-20, 1976.

Paasivirta, J., M. Knuutila, and R. Paukku. Study of organochlorine pollutants in snow at North Pole and comparison to the snow at north, central, and south Finland. Chemosphere, 14:1741-1748, 1985.

Pacyna, J.M., and M. Oehme. Long-range transport of some organic compounds to the Norwegian Arctic. Atmos. Environ., 22(2):243-257, 1988.

Pakarinen, P. Regional variation of sulphur concentrations in *Sphagnum* mosses and *Cladonia* lichens in Finnish bogs. Ann. Bot. Fenn., 18:275-279, 1981a.

Pakarinen, P. Anaerobic peat as a nutrient sink in raised bogs. Suo., 32:15-19, 1981b.

Pakarinen, P., and L. Tolonen. Studies on the heavy metal content of ombrotrophic *Sphagnum* species. Proc. 5th Int. Peat. Congr., Poznan, Poland, 1976. pp. 264-275, 1976a.

Pakarinen, P., and K. Tolonen. Regional survey of heavy metals in peat moss *Sphagnum*. Ambio, 5:38-40, 1976b.

Palazzo, A.J., and D.C. Leggett. Effect and disposition of TNT in a terrestrial plant. J. Environ. Qual., 15:49-52, 1986.

Parker, C. The importance of shoot entry in the action of herbicides applied to the soil. Weeds, 14:117-124, 1966.

Patterson, C.C. An alternative perspective - Lead pollution in the human environment: origin, extent, and significance. NAS, 1980:265-350, 1980.

Patton, G.W., D.A. Hinckley, M.D. Walla, T.F. Bidleman, and B.T. Hargrave. Airborne organochlorines in the Canadian high Arctic. Tellus, 41B:243-245, 1989.

Pauly, G., R. Douce, and J.P. Carde. Effects of β-pinene on spinach chloroplast photosynthesis. Z. Pflanzenphysiol., 104:199-209, 1981.

Payne, J.F. Mixed-function oxygenases in biological monitoring programs: Review of potential usage in different phyla of aquatic animals. In: G. Personne, E. Jaspers and C. Clares (eds.). Ecological Testing for the Marine Environment. State University of Ghant, Belgium, 1984. pp. 625-655.

Pearson, C.R. Halogenated aromatics. In: O. Hutzinger (ed.). The Handbook of Environmental Chemistry: Anthropogenic Compounds, Volume 3, Part B. Springer-Verlag, New York, 1982. pp. 89-116.

Pemadesa, M.A., and S. Korelege. Stomatal responses to 2,4-dinitrophenol. New Phytol., 78:573-578, 1977.

Percy, K.E. Heavy metal and sulfur concentrations in *Sphagnum* magellanicum Brid. in the Maritime Provinces, Canada. Water, Air, and Soil Pollut., 19:341-349, 1983.

Percy, K.E., and S. Borland. A multivariate analysis of element concentrations in *Sphagnum magellanicum* Brid. in the maritime provinces, Canada. Water Air Soil Pollut., 25:331-338, 1985.

Perera, F.P., M.C. Poirer, S.H. Yuspa, J. Nakayama, A. Jaretzki, M.M. Curnen, D.M. Knowles, and I.B. Weinstein. A pilot project in molecular cancer epidemiology: Determinatioin of B[a]P-DNA adducts in animal and human tissue by immunoassay. Carcinogenesis, 3:1405-1410, 1982.

Persson, B.R. Pb-210 atmospheric deposition in lichen-carpets in northern Sweden during 1961-1969. Tellus, 22:564-571, 1970.

Petersson, G. High ambient concentrations of monoterpenes in a Scandinavian pine forest. Atmos. Environ., 22:2617-2619, 1988.

Pimentel, D., and L. Levitan. Pesticides: Amounts Applied and Amounts Reaching Pests. BioScience, 36:86, 1986.

Pinder, J.E., III, and K. W. McLeod. Contaminant transport in agroecosystems through retention of soil particles on plant surfaces. J. Environ. Qual., 17:602-607, 1988.

Preiss, U., P.R. Wallnöfer, G. Engelhardt, and W. Mücke. Metabolism of 4-nitrophenol in cell suspension cultures of tomatoes. Toxicol. Environ. Chem., 19:87-92, 1989.

Prendeville, G.N. Shoot zone uptake of soil applied herbicides. Weed Res., 8:104-114, 1968.

Press, M.C., J. Henderson, and J.A. Lee. Arylsulphatase activity in peat in relation to atmospheric deposition. Soil Biol. Biochem., 1985.

Press, C.M., and J.A. Lee. Nitrate reductase activity of *Sphagnum* species in the south Pennines. New Phytol., 92:487-494, 1982.

Press, M.C., S.J. Woodin, and J.A. Lee. The potential importance of an increased atmospheric nitrogen supply to the growth of ombrotrophic *Sphagnum* species. New Phtytol., 103:45-55, 1986.

Price-Haughey, J., K. Bonham, and L. Gedamu. Heavy metal-induced gene expression in fish and fish cell lines. Environ. Health Perspec., 65:141-147, 1986.

Puckett, K.J. Bryophytes and Lichens as Monitors of Metal Deposition. In: T.H. Nash III, and V. Wirth, (eds.). Lichens, Bryophytes and Air Quality, J. Cramer, Berlin, 1988. pp. 231-267.

Puckett, K.J., and M.A.S. Burton. The Effect of Trace Elements on Lower Plants. In: N.W. Lepp (ed.). Effect of Heavy Metal Pollution on Plants, Vol. 2. Metals in the Environment, Applied Science Publishers, London, 1981. pp. 213-238.

Puckett, K.J., and E.J. Finegan. An analysis of the element content of lichens from the Northwest territories, Canada. Can. J. Bot., 58:2073-2089, 1980.

Rajagopal, V., and T.M. Rao. Effect of insecticide-weedicide (thimet and atrazine) application on nitrification in red soil and uptake of nitrogen. Pesticides, 18:47-50, 1984.

Rapaport, R.A., and S.J. Eisenreich. Atmospheric deposition of toxaphene to eastern N. America derived from peat accumulation. Atmos. Environ., 20:2367-2379, 1986.

Rapaport, R.A., and S.J. Eisenreich. Historical atmospheric inputs of high molecular weight chlorinated hydrocarbons in eastern North America. Environ. Sci. Technol., 22:931-941, 1988.

Rapaport, R.A., N.R. Urban, P.D. Capel, J.E. Baker, B.B. Looney, S.J. Eisenreich, and E. Gorham. New DDT inputs to North America: Atmospheric Deposition. Chemosphere, 14:1167-1173, 1985.

Ratsch, H.C., D.J. Johndro, and J.C. McFarlane. Growth inhibition and morphological effects of several chemicals in Arabidopsis thaliana (L.) Heynh. Environ. Toxicol. Chem., 5:55-60, 1986.

Ravanel, P., T. Taillandier, and M. Tissat. Uncoupling properties of a chlorophenol series on Acer cell suspensions: a QSAR study. Ecotoxicol. and Environ. Saf., 18:337-345, 1989.

Reich, P.B. Quantifying plant response to ozone: a unifying theory. Tree Physiol., 3:63-91, 1987.

Reinert, J. Der Einfluss Von 3,4-Benzpyren auf das Flachenwachstum und den Auxinspiegel der Prothallien von Stenochlaena Palustris. Z. Bot., 40:187-192, 1952.

Reischl, A., M. Reissinger, H. Thoma, and O. Hutzinger. Accumulation of organic air constituents by plant surfaces, Part IV. Plant surfaces: a sampling system for atmospheric polychlorodibenzo-p-doxin (PCDD) and polychllorodibenzo-p-furan (PCDF). Chemosphere, 18:561-568, 1989a.

Reischl, A., M. Reissinger, H. Thoma, and O. Hutzinger. Uptake and accumulation of PCDD/F in terrestrial plants: basic considerations. Chemosphere, 19:467-474, 1989b.

Reynolds, T. Comparative effects of aromatic compounds on inhibition of lettuce fruit germination. Ann. Bot., (NS). 42:15-23, 1978.

Rice, C.P., P.J. Samson, and G.E. Noguchi. Atmospheric transport of toxaphene to Lake Michigan. Environ. Sci. Tech., 20:1109-1111, 1986.

Richardson, C.J. Mechanisms controlling phosphorus retention capacity in freshwater wetlands. Science, 228:1424-1427, 1985.

Richardson, C.J., DiGiulio, R.T., and N.E. Tandy. Free-radical mediated processes as markers of air pollution in trees. In: Proceedings of the Workshop on Markers of Air Pollution Effects in Forests. April 25-27, 1988. Little Switzerland, North Carolina. National Research Council, Washington, DC, 1989.

Richardson, N. The mineral magnetic record in recent ombrotrophic peat synchronised by fine resolution pollen analysis. Phys. Earth and Planet. Inter., 42:48-56, 1986.

Rickard, D.T., and J.O. Nriagu. Aqueous Environmental Chemistry of Lead. In: J.O. Nriagu (ed.). Biogeochemistry of Lead in the Environment, Part A. Elsevier/North Holland, New York, Chapter 8, 1978.

Rippen, G., E. Zietz, R. Frank, T. Knacker, and W. Klopfer. Do airborne nitrophenols contribute to forest decline? Environ. Technol. Lett., 8:475-482, 1987.

Roberts, J.M., C.J. Hahn, F.C. Fehsenfeld, M.M. Warnock, D.L. Albritton, and R.E. Sievers. Moncterpene hydrocarbons in the nighttime troposphere. Environ. Sci. Technol., 19:364-369, 1985.

Robinson, N.J., and P.J. Jackson. "Metallothionein-like" metal complexes in angiosperms; their structure and function. Physiol. Plant., 67:499-506, 1986.

Rovira, A.D. Plant root exudates. Bot. Rev., 35:35-57, 1969.

Royce C.L., J.S. Fletcher, P.R. Risser, J.C. McFarlane, and F.E. Benenati. PHYTOTOX: A database dealing with the effect of organic chemicals on terrestrial vascular plants. J. Chem. Inf. Comput. Sci., 24:7, 1984.

Rudolph, H., and J.V. Voight. Effects of NH_4-N and NO_3-N on growth and metabolism of *Sphagnum magellanicum*. Physiol. Plant., 66:339-343, 1986.

Ruhling, A., and G. Tyler. Sorption and retention of heavy metals in the woodland moss *Hylocomium splendens* Br. et Sch. Oikos, 21:92-97, 1970.

Ruhling, A., and G. Tyler. Recent changes in the deposition of heavy metals in northern Europe. Water, Air, and Soil Pollut., 22:173-180, 1984.

Ryan, J.A., R.M. Bell, J.M. Davidson, and G.A. O'Connor. Plant uptake of non-ionic organic chemicals from soils. Chemosphere, 17:2299-2323, 1988.

Rydberg, B. The rate of strand separation in alkali of DNA or irradiated mammalian cells. Radiat. Res., 61:274-287, 1975.

Sacchi, G.A., P. Vigano, G. Fortunati, and S.M. Cocucci. Accumulation of 2,3,7-8-tetrachlorodibenzo-p-dioxin from soil and nutrient solution by bean and maize plants. Experientia, 42:586-588, 1986.

Santelmann, M.V., and E. Gorham. The influence of airborne road dust on the chemistry of *Sphagnum* mosses. J. Ecol., 76:1219-1231, 1988.

Sapek, A. Contamination of peat soils with lead and cadmium. Int. Peat Congr., 1976. pp. 284-294.

Sargent, J.A. Relationship of selectivity to uptake and movement. In: L.J. Audus (ed.). Herbicides: Physiology, Biochemistry, Ecology. Vol. 2. Academic Press, London, 1976. pp. 303-312.

Sargent, J.A., and G.E. Blackman. Studies on foliar penetration. I. Factors controlling the entry of 2,4-dichlorophenoxyacetic acid. J. Exp. Bot., 13:348-368, 1962.

Sawicki, E., W.C. Elbert, T.R. Hauser, F.T. Fox, and T.W. Stanley. Benzo(a)pyrene content of the air of American communities. American Industrial Hygienists Association Journal, 21:443-451, 1960.

Schaefer, D.A., S.E. Lindber, and W.A. Hoffman, Jr. Fluxes of undissociated acids to terrestrial ecosystems. Tellus, 41B:207-218, 1989.

Scheunert, I., C. Bin, and F. Korte. Fate of 2,4,6-trichlorphenol-^{14}C in a laboratory soil-plant system. Chemosphere, 19:1715-1720, 1989.

Scheunert, I., Z. Qiao, and F. Korte. Comparative studies of the fate of atrazine-^{14}C and pentachlorophenol-^{14}C in various laboratory and outdoor soil-plant systems. J. Environ. Science and Health, B21:457-485, 1986.

Scheunert, I., E. Topp, J. Schmitzer, W. Klein, and F. Korte. Formation and fate of bound residues of [^{14}C]benzene and [^{14}C]chlorobenzenes in soil and plants. Ecotoxicol. and Environ. Saf., 9:159-170, 1985.

Schmitzer, J.L., I. Scheunert, and F. Korte. Fate of di(2-ethylhexyl)pthalate 14-C in laboratory and outdoor soil-plant systems. J. Agric. Food Chem., 36:210-215, 1988.

Schreiber, R.K. Influence of Airborne Pollutants on Forest Wildlife. In: Air Pollutants Effects on Forest Ecosystems. The Acid Rain Foundation. St. Paul, MN, 1985.

Schroder, P., and H. Rennenberg. Glutathione-S-transferases in spruce needles: enzymes for the detoxification of airborne xenobiotics. In: International Congress on Forest Decline Research: State of Knowledge and Perspectives. Forschungsbeirat Waldschaden/Luftverunreinigungen der Bundesregierung und der Lander, Lake Constance, West Germany, 1989. pp. 423-424.

Schroeder, W.H., and D.A. Lane. The fate of toxic airborne pollutants. Environ. Sci. Technol., 22:240-246, 1988.

Schulze, E.D. Air pollution and forest decline in a spruce (*Picea abies*) forest. Science, 244:776-783, 1989.

Schwartzman, D., M. Kasim, L. Stelff, and J.J. Johnson, Jr. Quantitative monitoring of airborne lead pollution by foliose lichen. Water, Air, and Soil Pollut., 32:363-378, 1987.

Scoullos, M.J., and J. Hatzianestis. Dissolved and particulate trace metals in a wetland of international importance: Lake Mikri Prespa, Greece. Water, Air, and Soil Pollut., 44:307-320, 1989.

Seaward, M.R.D. Lichen ecology of the scunthorpe heathlands. I. Mineral accumulation. Lichenologist, 5:423-433, 1973.

Sericano, J.L, and A.E. Pucci. Chlorinated hydrocarbons in the seawater and surface sediments of Blanca Bay, Argentina. Estuarine, Coastal and Shelf Science, 19:27-51, 1984.

Settle, D.M., and C.C. Patterson. Lead in albacore: guide to lead pollution in Americans. Science, 207:1167, 1980.

Shabad, L.M. Circulation of carcinogenic polycyclic aromatic hydrocarbons in the human environment and cancer prevention. J. Natl. Cancer Inst., 64:405-410, 1980.

Shabad, L.M., Y.L. Cohan, A.P. Ilnitsky, A.Y. Khesina, N.P. Shcherbak, and G.A. Smirnov. The carcinogenic hydrocarbon benzo[a]pyrene in the soil. J. Natl. Cancer Inst., 47:1179-1191, 1971.

Shabad, L.M., and Y.L. Cohan. The contents of benzo[a]pyrene in some crops. Arch. Geschwulstforsch., 40:237-243, 1972.

Shafer, W.E., and J. Schonherr. Accumulation and transport of phenol, 2-nitrophenol, and 4-nitrophenol in plant cuticles. Ecotoxicol. and Environ. Saf., 10:239-252, 1985.

Shah, J.J., and H. B. Singh. Distribution of volatile organic chemicals in outdoor and indoor air. Environ. Sci. Technol., 22:1381-1385, 1988.

Shea, P.J., J.B. Weber, and M.R. Overcash. Uptake and phytotoxicity of di-n-butyl phtalate in corn (Zea mays). Bull. Environ. Contam. Toxicol., 29:153-158, 1982.

Shea, P.J., J.B. Weber, and M.R. Overcash. Biological activities of 2,4-dinitrophenol in plant-soil systems. Residue Reviews, 87:1-41, 1983.

Sheppard, M.I., and S.H. Thibault. Migration of technetiuum, iodine, neptunium, and uranium in the peat of two minerotrophic mires. J. Environ. Qual., 17:644-653, 1988.

Shirahata, H., R.W. Elias, and C.C. Patterson. Chronological variations in concentrations and isotopic compositions of anthropogenic atmospheric lead in sediments of a remote subalpine pond. Geochem. Cosmochem. Acta., 44:149, 1980.

Shone, M.G.T., B.O. Bartlett, and A.V. Wood. A comparison of the uptake and translocation of some organic herbicides and a systemic fungicide by barley. II. Relationship between uptake by roots and translocation to shoots. J. Exper. Bot., 25:401-409, 1974.

Shone, M.G.T., D.T. Clarkson, J. Sanderson, and A.V. Wood. A Comparison Of the Uptake and Translocation of Some Organic Molecules and Ions in Higher Plants. In: W.P. Anderson (ed.) Ion Transport in Plants. Academic Press, London, 1973. pp. 571-582.

Shone, M.G.T., and A.V. Wood. A comparison of the uptake and translocation of some organic herbicides and a systemic fungicide by barley. I. Absorption in relation to physico-chemical properties. J. Exp. Bot., 25:390-400, 1974.

Shone, M.G.T., and A.V. Wood. Uptake and translocation of some pesticides by hypocotyls of radish seedlings. Weed Res., 16:229-238, 1976.

Shortle, W.C., and K.T. Smith. Aluminum-induced calcium deficiency syndrome in declining red spruce. Science, 240:1017-1018, 1988.

Shugart, L.R. Quantitating exposure to chemical carcinogens: *In vivo* alkylation of hemoglobin by benzo[a]pyrene. Toxicol. 34:211-220, 1985a.

Shugart, L.R. Covalent binding of B[a]P-diolepoxide to DNA of mouse skin: *In vivo* persistence of adducts formation. J. Toxicol. Environ. Health., 15:255-263, 1985b.

Shugart, L.R. Quantifying adductive modification of hemoglobin from mice exposed to benzo[a[pyrene. Anal. Biochem., 152:365-369, 1986.

Shugart, L.R. Quantitation of chemically induced damage to DNA of aquatic organisms by alkaline unwinding assay. Aquat. Toxicol., 13(1):43-52, 1988.

Shugart, L.R., J.M. Holland, and R. Rahn. Dosimetry of PAH skin carcinogenesis: Covalent binding of benzo[a]pyrene to mouse epidermal DNA. Carcinogenesis, 4:195-199, 1983.

Shugart, L.R., and J. Kao. Examination of adduct formation *in vivo* in the mouse between BaP and DNA of skin and hemoglobin of red blood cells. Environ. Health Perspec., 62:223-226, 1985.

Shugart, L.R., J.F. McCarthy, B.D. Jimenez, and J. Daniels. Analysis of adduct formation in bluegill sunfish (*Lepomis macrochiris*) between benzo[a]pyrene and DNA of the liver and hemoglobin of the erythrocyte. Aquatic Toxicol., 9(6):319-325, 1987.

Shugart, L.R., S.M. Adams, B.D. Jimenez, S.S. Talmage, and J.F. McCarthy. Biological markers in animals can provide information on exposure and bioavailability of environmental contaminants. In: R. Wang and C. Franklin (eds.). Chemical Basis for Monitoring. American Chemical Society Symposium Series. Washington, DC, 1989.

Siccama, T.G., W.H. Smith, and D.L. Mader. Changes in lead, zinc, copper, dry weight, and organic matter content of the forest floor of white pine stands in central Massachusetts over 16 years. Environ. Sci. Technol., 15:54, 1980.

Siddaramappa, R., and I. Watanabe. Evidence for vapor loss of ^{14}C-carbofuran from rice plants. Bull. Environ. Contam. Toxicol., 23:544-551, 1979.

Simon, E.W., and H. Beevers. The effect of pH on the biological activities of weak acids and bases. I. The most usual relationship between pH and activity. New Phytol., 51:163-190, 1951.

Simon, W.E., H.A. Roberts, and G.E. Blackman. Studies in the principles of phytotoxicity. III. The pH factor and the toxicity of 3:5-dinitro-o-cresol, a weak acid. J. Exp. Bot., 3:99-109, 1952.

Singh, M., and J.R. Orsenigo. Phytotoxicity of nonionic surfactants to sugarcane. Bulletin of Environ. Contam. Toxicol., 32:119-124, 1984.

Skiba, U., M.S. Cresser, R.G. Derwent, and D.W. Futty. Peat acidification in Scotland. Nature, 337:68-69, 1989.

Sladek, N.E., and G.J. Mannering. Evidence for a new P-450 hemoprotein in hepatic microsomes from methylcholanthrene treated rats. Biochem. Biophys. Res. Commun., 24:668-674, 1966.

Smith, D., and K.P. Buchholtz. Modification of plant transpiration rate with chemicals. Plant Physiol., 39:572-578, 1964.

Smith, A.E., R. Grover, A.J. Cessna, S.R. Shewchuk, and J.H. Hunter. Fate of diclofop-methyl after application to a wheat field. J. Environ. Qual., 15:234-238, 1986.

Smith, W.H., and T.G. Siccama. The Hubbard Brook ecosystem study: biogeochemistry of lead in the northern hardwood forest. J. Environ. Qual., 10:323, 1981.

Sodergren, A. Chlorinated hydrocarbon residues in airborne fallout. Nature, 236:395-397, 1972.

Sparling, J. The occurrence of *Schoenus nigricans* L. in blanket bogs. II. Experiments on the growth of *S. nigricans* under controlled conditions. J. Ecol., 55:15-31, 1967.

Spencer, W.F., M.M. Cliath, W.A. Jury, and L.-Z. Zhang. Volatilization of organic chemicals from soil as related to their Henry's Law constants. J. Environ. Qual., 17:504-509, 1988.

Stangl, H., D. Kotzias, and F. Geiss. The role of terpenes in the dry deposition of ozone and ozone/sulfur dioxide mixtures. Naturwissenschaften, 75:42-43, 1988.

Stanley, C.W., J.E. Barney, M.R. Helton, and A.R. Yobs. Measurements of atmospheric levels of pesticides. Environ. Sci. Technol., 5:430-435, 1971.

Steffens, W., and J. Wieneke. Influence of humidity and rain on uptake and metabolism of ^{14}C-azinphos-methyl in bean plants. Arch. Environ. Contam. Toxicol., 3:364-370, 1975.

Suess, M.J. The environmental load and cycle of polycyclic aromatic hydrocarbons. Sci. Total Environ., 6:239-250, 1976.

Sund, K.A., and N. Nomura. Laboratory evaluation of several herbicides. Weed Res., 3:35-43, 1963.

Sundstrom, G., A. Larsson, and M. Tarkpea. Creosote. In: O. Hutzinger (ed.). The Handbook of Environmental Chemistry: Anthropogenic Compounds, Volume 3, Part D. Springer-Verlag, New York, 1986. pp. 159-205.

Suzuki, M., N. Aizawa, G. Okano, and T. Takahashi. Translocation of polychlorobiphenyls in soil into plants: a study by a method of culture of soybean sprouts. Arch. Environ. Contam. Toxicol., 5:343-352, 1977.

Swackhamer, D.L, and D.E. Armstrong. Estimation of atmospheric and nonatmospheric contributions and losses of polychlorinated biphenyls for Lake Michigan on the basis of sediment records of remote lakes. Environ. Sci. Technol., 20:879-883, 1986.

Swindell, B.F., J.E. Smith, D.G. Neary, and N.B. Comerford. Recent research indicates plant community responses to intensive treatment including chemical amendments. South. J. Appl. For., 13:152, 1989.

Tallis, J.H. Studies on Southern Pennine peats: III. The behavior of *Sphagnum*. J. Ecol., 52:345-353, 1964.

Tanabe, S., H. Hidaka, and R. Tatsukawa. PCBs and chlorinated hydrocarbon pesticides in Antarctic atmosphere and hydrosphere. Chemosphere, 12(2):277-288, 1983.

Tanabe, S., and R. Tatsukawa. Chlorinated hydrocarbons in the North Pacific and Indian Oceans. J. Oceanogr. Soc. Jap., 36(4):217-226, 1980.

Tanabe, S., R. Tatsukawa, M. Kawano, and H. Hidaka. Global distribution and atmospheric transport of chlorinated hydrocarbons: HCH (BHC) isomers and DDT compounds in the western Pacific, eastern Indian and Antarctic Oceans. J. Oceanogr. Soc. Jap., 38(3):137-148, 1982.

Tanabe, S, and R. Tatsukawa. Vertical transport and residence time of chlorinated hydrocarbons in the open ocean water column. J. Oceanogr. Soc. Jap., 39(2):53-62, 1983.

Taylor, G.J., and A.A. Crowder. Accumulation of atmospherically deposited trace metals in wetland soils of Sudbury, Ontario. Water, Air, and Soil Pollut., 19:29-42, 1983.

Thomas, W. Ueber die Verwendung von Pflanzen zur Analyse raeumlicher Spurensubstanz-Immissionsmuster. Staub - Reinhalt. Lufthyg., 43:141-149, 1983.

Thomas, W. Accumulation of Airborne Trace Pollutants by Arctic Plants and Soil. Water Sci. Technol., 18:47, 1986.

Thomas, W., and R. Herrmann. Nachweis von Chlorpestiziden, PCB, PCA und Schwermetallen mittels epiphytischer Mosse als Biofilter entlang eines Profiles durch Mitteleuropa. Staub-Reinhalt. Lufthyg., 40:440-444, 1980.

Thompson, N. Diffusion and uptake [illegible] chemical vapor volatilizing from a sprayed target area. Pesticide Sci., 14:33, 1983.

Tilton, D.L. Comparative growth and foliar element concentrations of *Laris laricina* over a range of wetland types in Minnesota. J. Ecol., 66:499-512, 1978.

Tingey, D.T., Hites, R.C., and C. Wickliff. Differential foliar sensitivity of soybean cultivars to ozone associated with differential enzyme activities. Physiol. Plant., 37:69-72, 1976a.

Tingey, D.T., Wilhour, R. G., and C. Standley. The effect of chronic ozone exposures on the metabolite content of Ponderosa pine seedlings. For. Sci., 22:234-241, 1976b.

Tolonen, K., and F. Oldfield. The record of magnetic-mineral and heavy metal deposition of Regent Street Bog, Fredricton, New Brunswick, Canada. Phys. Earth Planet. Inter., 42:57-66, 1986.

Tomassini, F.D., K.J. Puckett, E. Nieboer, D.H.S. Richardson, and B. Grace. Determination of copper, iron, nickel and sulphur by x-ray fluorescence in lichens from the Mackenzie Valley, Northwest Territories, and the Sudbury District, Ontario. Can. J. Bot., 54:1591-1603, 1976.

Topp, E., I. Scheunert, A. Attar, and F. Korte. Factors affecting the uptake of ^{14}C-labeled organic chemicals by plants from soil. Ecotoxicol. Environ. Saf., 11:219-228, 1986.

Trainer, M., E.J. Williams, D.D. Parrish, M.P. Buhr, E.J. Allwine, H.H. Westberg, F.C. Fehsenfeld, and S.C. Liu. Models and observations of the impact of natural hydrocarbons on rural ozone. Nature, 329:705-707, 1987.

Travis, C.C., and H.A. Hattemer-Frey. Uptake of organics by aerial plant parts: a call for research. Chemosphere, 17:277-283, 1988.

Tucker, W.A., and A.L. Preston. Procedures for estimating atmospheric deposition properties of organic chemicals. Water, Air, and Soil Pollut., 21:247-260, 1984.

Tukey, H.B., Jr. The leaching of substances from plants. Ann. Rev. Plant Physiol., 21:305-324, 1970.

Turner, R.S., A.H. Johnson, and D. Wang. Biogeochemistry of lead in McDonalds Branch watershed, New Jersey Pine Barrens. J. Environ. Qual., 14:305-314, 1985.

U.S. Environmental Protection Agency. The Toxic Release Inventory: A National Perspective. U.S. Environmental Protection Agency, EPA560/4-89-005, Washington, DC, 1989.

Urban, N.R., and S.E. Bayley. The acid-base balance of peatlands: a short-term perspective. Water, Air, and Soil Pollut., 30:791-800, 1986.

Urban, N.R., S.E. Bayley, and S.J. Eisenreich. Export of dissolved organic carbon and acidity from peatlands. Water Resour. Res., 25:1619-1628, 1989a.

Urban, N.R., S.J. Eisenreich, and S.E. Bayley. The relative importance of denitrification and nitrate assimilation in mid-continental bogs. Limnol. and Oceanogr., 33:1611-1617, 1989b.

Urban, N.R., S.J. Eisenreich, and D.F. Grigal. Sulfur cycling in a forested *Sphagnum* bog in northern Minnesota. Biogeochem., 7:81-109, 1989c.

Urban, N.R., S.J. Eisenreich, and E. Gorham. Proton Cycling in bogs: Geographic variation in northeastern North America. In: T.C. Hutchinson and K.M. Meema (eds.). The Effects of Air Pollutants on Forests, Wetlands and Agricultural Ecosystems. Springer-Verlag, NY, 1987a. pp. 577-598.

Urban, N.R., S.J. Eisenreich, and E. Gorham. Aluminum, iron, zinc and lead in bog waters. Can. J. Fish. Aquat. Sci., 44:1165-1172, 1987b.

Urban, N.R., and S.J. Eisenreich. The nitrogen cycle of a *Sphagnum* bog. Can. J. Bot., 66:435-449, 1988.

Urban, N.R., and S.K. Eisenreich. Sulfur metabolism and organic acids: implications for the natural and anthropogenic acidification of peatlands and colored lakes. Rep. to Water Resources Res. Ctr., Minneapolis, MN, 1989.

van Andel, O.M., W. van der Zweep, and C.J. Gorter. Morphogenetic responses of plants. In: L.J. Audus, (ed.). Herbicides: Physiology, Biochemistry, Ecology. Vol. 1. Academic Press, Londo, 1976. pp. 127-164.

van Auken, O.W., and M. Hulse. Translocation, distribution, and environmental degradation of hexachlorophene in tomatoes. Arch. Environ. Contam. Toxicol., 8:213-230, 1979.

van der Valk, A.G., C.B. Davis, J.L. Baker, and C.E. Beer. Natural freshwater wetlands as nitrogen and phosphorus traps for land runoff. In: P.E. Greeson, J.R. Clark, J.E. Clark (eds.). Wetland Functions and Values: The State of Our Understanding, 1978. pp. 457-467.

van Haut, V.H., and B. Prinze. Beurteilung der relativen Pflanzenschädlichkeit organischer Luftverunreinigungen im LIS-Kurzzeittest. Staub-Reinhalt. Luft, 39:408-414, 1979.

van Oorschot, J.L.P. Effects in relation to water and carbon dioxide exchange of plants. In L.J. Audus, (ed.). Herbicides: Physiology, Biochemistry, Ecology. Vol. 1. Academic Press, London, 1976. pp. 305-334.

van Overbeek, J., and R. Blondeau. Mode of action of phytotoxic oils. Weeds, 3:55-65, 1954.

Verhoeven, J.T., S. van Beek, M. Dekker, and W. Storm. Nutrient dynamics in small mesotrophic fens surrounded by cultivated land. Oecol., 60:25-33, 1983.

Verhoeven, J.T.A., A.M. Kooijman, and G. van Wirdum. Mineralization of N and P along a trophic gradient in a freshwater mire. Biogeochem., 6:31-44, 1988.

Verhoeven, J.T.A., E. Maltby, and M. B. Schmitz. Nitrogen and phosphorus mineralization in fens and bogs. J. Ecol., 1990.

Vestergaard, N.K., U. Stephansen, and L. Rasmussen. Airborne heavy metal pollution in the environment of a Danish steel plant. Water, Air, and Soil Pollut., 27:363-377, 1986.

Waddel, T.E., and B.T. Bower. Managing Agricultural Chemicals in the Environment: The Case for a Multimedia Approach. The Conservation Foundation, Washington, DC, 1988. pp. 42-43.

Wagner, E., H.-J. Klingler, J. Franzen, and K. Gross. Physiology and pathophysiology of monoterpenes in modern forest decline. Bull. Ecol. Soc. Am., 70:289, 1989.

Wain, R.L., and M.S. Smith. Selectivity in relation to metabolism. In: L.J. Audus (ed.). Herbicides: Physiology, Biochemistry, Ecology. Vol. 2. Academic Press, London, 1976. pp. 279-302.

Wang, D.T., and O. Meresz. Occurrence and Potential Uptake of Polynuclear Aromatic Hydrocarbons of Highway Traffic Origin by Proximally Grown Food Crops (Abstract). Sixth International Symposium on PAH, Battelle Columbus Laboratories, Columbus, Ohio, 1981. 117 pp.

Warner, M.L., R.H. Sauer, and D.W. Carlile. Barley growth in coal liquid and diesel liquid fuels from coal and oil: a comparison of potential toxic effects on barley. Water, Air, and Soil Pollut. 22:47-55, 1984.

Washburn, P.C., and R.T. DiGiulio. Stimulation of superoxide production by nitrofurantoin, p-nitrobenzoic acid and m-dinitrobenzene in hepatic microsomes of three species of freshwater fish. Environ. Toxicol. Chem., 8:171-180, 1989.

Watt, R.F., and M.L. Heinselman. Foliar nitrogen and phosphorus level related to site quality in a northern Minnesota spruce bog. Ecology, 46:357-360, 1965.

Webb, M. The metallothioneins. In: The chemistry, biochemistry, and biology of cadmium. Elseview/North-Holland Biomedical Press. New York., 1979. pp. 195-266.

Weber, J.B., and E. Mrozek, Jr. Polychlorinated biphenyls: phytotoxicity, absorption and translocation by plants, and inactivation by activated carbon. Bull. Environ. Contam. Toxicol., 23:412-417, 1979.

Wedding, R.T., and L.A. Riehl. Influence of petroleum oil on the translocation of phosphorus in small lemon plants. Am. J. Bot., 45:138-142, 1958.

Weinstein, D.A., and E.M. Birk. The effects of chemicals on the structure of terrestrial ecosystems: mechanisms and patterns of change. In: S.A. Levin, M,A, Harwell, J.R. Kelly, K.D. Kimball, eds. Ecotoxicology: Problems and Approaches, Springer-Verlag, New York, 1989. pp. 181-212.

Weiss, H.H., M. Koide, and E.D. Goldberg. Selenium and sulfur in a Greenland ice sheet: relation to fossil fuel combustion. Science, 172:261-263, 1971.

Wettig, K., G. Gelbert, L.M. Shabad, and A.Y. Khesina. Benzo[a]pyrene determination in plant seeds before and after germination. Vopr. Onkol., 22:51-54, 1976.

Wickliff, C., J.C. McFarlane, and H. Ratsch. Uptake of bromacil by isolated barley roots. Environmental Monitoring and Assessment, 4:43-51, 1984.

Wickstrom, K., and K. Tolonen. The history of airborne polycyclic aromatic hydrocarbons (PAH) and perylene as recorded in dated lake sediments. Water, Air, and Soil Pollut., 32:155-175, 1987.

Wieder, R.K., and G.E. Lang. Modification of acid mine drainage in a freshwater wetland. Symposium on Wetlands of the Unglaciated Appalachian Region, W. Va. Univ. Morgantown, W. Va., 1982. pp. 43-53.

Wieder, R.K., and G.E. Lang. Fe, Al, Mn, and S chemistry of *Sphagnum* peat in four peatlands with different metal and sulfur input. Water, Air, and Soil Pollut., 29:309-320, 1986.

Wilcox, D.A., R.J. Shedlock, and W.H. Hendrickson. Hydrology, water chemistry and ecological relations in the raised mound of Cowles Bog. J. Ecol., 74:1103-1117, 1986.

Willis, G.H., L.L. McDowell, S. Smith, and L.M. Southwick. Permethrin washoff from cotton plants by simulated rainfall. J. Environ. Qual., 15:116-120, 1986.

Winner, W.E., and C.J. Atkinson. Annual absorption of gaseous air pollutants by mosses and vascular plants in diverse habitats. In: T.C. Hutchinson and K.M. Meema (eds.). Effects of Atmospheric Pollutants on Forests, Wetlands and Agricultural Ecosystems. Springer, Berlin, 1987. pp. 427-438.

Wolfenden, J., D.C. Robinson, J.N. Cape, I.S. Paterson, B.J. Francis, H. Mehlhorn, and A.R. Wellburn. Use of carotenoid ratios, ethylene emissions and buffer capacities for the early diagnosis of forest decline. New Phytol., 109:85-95, 1988.

Wolverton, B.C., R.C. McDonald, and E.A. Watkins, Jr. Foliage plants for removing indoor air pollutants from energy efficient houses. Econ. Bot., 38:224, 1984.

Wood, B.W., J.A. Payne, and T.R. Gottwald. Inhibition of photosynthesis in pecan leaves by fungicides. Plant Disease, 69:997-998, 1985.

Wood, B.W., and J. A. Payne. Net photosynthesis of orchard grown pecan leaves reduced by insecticide sprays. HortScience, 21:112-113, 1986.

Woodin, S.J.U., and J.A. Lee. The fate of some components of acidic deposition in ombrotrophic mires. Environ. Pollut., 45:61-72, 1987.

Woodin, S., M.C. Press, and J.A. Lee. Nitrate reductase activity in *Sphagnum fuscum* in relation to wet deposition of nitrate from the atmosphere. New Phytol., 99:381-388, 1985.

Xun, L., N.E.R. Campbell, and J.W.M. Rudd. Measurements of specific rates of net methyl mercury production in the water column and surface sediments of acidified and circumneutral lakes. Can. J. Fish. Aquat. Sci., 44:750-757, 1987.

Yates, W.E., N.B. Akesson, and D.E. Bayer. Drift of glyphosate sprays applied with aerial and ground equipment. Weed Sci., 26:597, 1978.

Yavitt, J.B., G.E. Lange, and R.K. Wieder. Control of carbon mineralization to CH_4 and CO_2 in anaerobic, *Sphagnum*-derived peat from Big Run Bog, West Virginia. Biogeochem., 4:141-158, 1987.

Zander, M. Polycyclic aromatic and heteroaromatic hydrocarbons. In: O. Hutzinger (ed.). The Handbook of Environmental Chemistry: Anthropogenic Compounds, Volume 3, Part A. Springer-Verlag, New York, 1980. pp. 109-131.

Zeigler, I. The effect of SO_2 on the activity of ribulose-l,5-diphosphate carboxylase in spinach chloroplasts. Planta, 103:155-163, 1972.

Zoltai, S.C. Distribution of base metals in peat near a smelter at Flin Flon, Manitoba. Water, Air, and Soil Pollut., 37:217-230, 1988.

Zweig, A., and G.W. Nachtigall. Photo-sensitized herbicidal action. Photochemistry and Photobiology, 22:257-259, 1975.